PHASE RELATIONSHIPS AND LONG-TERM TEMPERATURE STABILITY IN THE HIGH ZIRCONIA REGION OF THE CALCIA-ALUMINA-ZIRCONIA SYSTEM

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PHASE RELATIONSHIPS AND LONG-TERM TEMPERATURE STABILITY

IN THE HIGH ZIRCONIA REGION OF THE

CALCIA-ALUMINA-ZIRCONIA SYSTEM

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SUMMARY

The phase diagram of the calcia-alumina-zirconia ternary system in the high zirconia region was determined by the disappearing phase method. Qualitative and quantitative X-ray analysis was used to determine the phases present in samples that had been fired to 1500 °C and 1700 °C. Optical analysis was used to determine the total calcium aluminates and zirconia phase contents by volume. Results indicated that CA_2 may exhibit solid solution characteristics giving it a stoichiometry as high as C_3A_7. Solid solution was also observed in the cubic zirconia phase. A small portion of alumina entered the zirconia lattice, as well as 11.2 to 14.6 mole percent calcia in the completely stabilized zirconia phase. No quantitative determination could be made of the amount of calcia or alumina present in the monoclinic zirconia lattice. Considerable melting occurred in the samples fired at 1700 °C which led to a non-equilibrium state on cooling and thus made phase equilibria determinations questionable.

Samples were fired at 1550 °C to be used for the study of long term phase stability. When held at 1300 °C, cubic zirconia destabilization occurred with time and 800 to 1000 hours were required to reach equilibrium. However, at 900 °C destabilization occurred very slowly and was not nearly complete after 2000 hours. Lattice parameter measurements indicated approximately two mole percent more calcia in the cubic zirconia structure at equilibrium at 1300 °C than at 1550 °C.

GLOSSARY OF ABBREVIATIONS

CA	$CaO \cdot Al_2O_3$
CA_2	$CaO \cdot 2Al_2O_3$
C_3A_5	$3CaO \cdot 5Al_2O_3$
CA_6	$CaO \cdot 6Al_2O_3$
CZ	$CaO \cdot ZrO_2$
C_3A_7	$3CaO \cdot 7Al_2O_3$
SS	Solid Solution
C_7A_3Z	$7CaO \cdot 3Al_2O_3 \cdot ZrO_2$

CHAPTER I

INTRODUCTION

A refractory of high zirconia content stabilized with both calcia and alumina may become useful in the coal gasification industry because of good corrosion resistant characteristics of the components. No complete phase diagram of this portion of the ternary system is available. In order to prepare such a phase diagram, samples of various compositions in the system were mixed and fired. X-ray and optical analysis of the resulting phases permitted determination of compatibility triangles. Because of the cubic zirconia solid solution phase and also because of the possibility of a solid solution of CA_2, particular attention was required to determine the changing compositions as temperature of firing varied.

From a practical point of view, the quantity of phase change at different temperatures with long use must be determined if such a material were to be used as a refractory. Because of the thermal shock problems involved in the transition from tetragonal to monoclinic zirconia, it is especially important to know quantitatively the increase in the amount of monoclinic zirconia with time. This was studied by firing for up to 2000 hours at 900 ^{o}C and 1300 ^{o}C.

CHAPTER II

SURVEY OF LITERATURE

Little information has been published for the $CaO-Al_2O_3-ZrO_2$ ternary system and no phase diagram of the high zirconia region has been published detailing the solid solution and polymorphic information. Only Berezhnoi[1] in Russia has published information directly relating to the ternary phase diagram.

In order to gain an understanding of the system from the literature one must study reports about the three binary systems that are involved: ZrO_2-CaO, Al_2O_3-CaO, and $Al_2O_3-ZrO_2$. The first two of these systems have been well studied, although there remains much contradiction. The third system forms no binary compounds and is thus less complex.

$CaO-Al_2O_3-ZrO_2$

Berezhnoi[1] has published the only available phase diagram of the ternary system $CaO-Al_2O_3-ZrO_2$, Figure 1. He was primarily interested in the new ternary compound which he had discovered, $Ca_7Al_6ZrO_{18}$, which is a potential hydraulic binder[2], and thus he did not look at polymorphs of zirconia or at the solid solution structure of zirconia.

$Ca_7Al_6ZrO_{18}$ was found to be a useful binder in the hydrated state. It is the first known substance containing ZrO_2 to exhibit such properties, according to Berezhnoi. The new compound was prepared from high purity silica chalk, technical grade alumina, and zirconia which were mixed and fired to a temperature of 1400 °C to 1460 °C. Synthesis required one

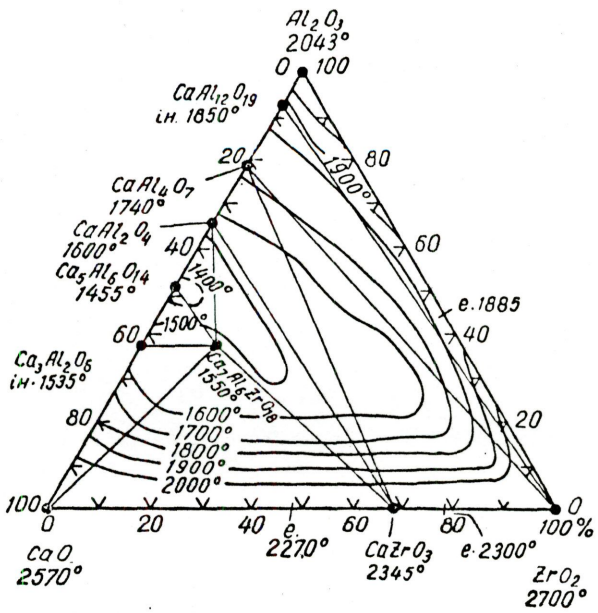


Figure 1. Phase Diagram of the CaO-Al_2O_3-ZrO_2 System as Determined by Berezhnoi[1]

hour at 1450 °C. It melts incongruently at 1550 °C (with the formation of $CaZrO_3$), has a density of 3.1 g/cc, and a linear thermal expansion coefficient of 8.7×10^{-6}/°C (20-1000 °C). X-ray d spacing information is reproduced in Table 1.

Table 1. X-ray d Spacings[2] for $Ca_7Al_6ZrO_{18}$

d (A)	I	d (A)	I	d (A)	I
7.61	10	2.218	6	1.829	12
4.10	10	2.177	6	1.669	5
3.42	29	2.114	4	1.647	6
3.36	10	2.081	5	1.628	5
2.758	10	1.945	5	1.565	19
2.696	100	1.918	16	1.555	10
2.647	26	1.889	22	1.537	11
2.305	5	1.863	12	1.507	5

Tarnopol'skaya and Gul'ko[3] have published some basic information concerning the quaternary system $CaO\text{-}SrO\text{-}Al_2O_3\text{-}ZrO_2$. Their investigation was limited to studying the compounds present in the system and possible uses of them as refractories. They confirmed the existence of $Ca_7Al_6ZrO_{18}$ but presented no other information useful to the study of the ternary.

N. I. Voronin[4] commented that an alumina impurity in zirconia may improve the heat resistance of zirconia when it is stabilized with magnesia, but apparently he did not work with calcia stabilized zirconia.

Antonio Cocco[5] reported that up to three percent alumina could enter the structure of calcia stabilized zirconia without affecting that structure. His work was at temperatures from 1400 °C to 1700 °C but only compositions of more than 29 mole percent calcia were investigated, which limited his study to the phase region of cubic zirconia and $CaZrO_3$.

Takagi[6] investigated the effect of alumina on the sintering of

calcia stabilized zirconia. For raw materials he used zirconium oxychloride, calcium carbonate, and aluminum nitrate. Sixteen mole percent calcia was used to stabilize the zirconia phase. The samples were fired in air at 1700 °C for one hour. He discovered that the addition of from 0.5 to 4 weight percent of alumina enhanced the sintering of the zirconia. The zirconia grain size was about 50 microns for additions of from two to four weight percent alumina. At 1700 °C Takagi observed some liquid phase sintering. The only calcium aluminate phase observed was CA_6 in both scanning electron microscope analysis and electron probe X-ray microanalysis.

ZrO_2-CaO

Zirconia has a melting point of 2680 ± 20 °C and therefore would appear to be very useful as a refractory,[7] especially since it has good corrosion resistance and high strength. Its density is 5.89 g/cc. It has low thermal conductivity and does not react with most metals nor is it easily wetted by molten glass. However, at 1000 °C there is a destructive transformation which makes zirconia a poor refractory in its pure state. Below 1000 °C zirconia has a monoclinic crystal structure. At 1000 °C it transforms rapidly into a tetragonal structure with a significant density change and thus destructive thermal expansion. Figure 2 shows the effect of heating zirconia through this tranformation.

To combat this transformation in zirconia which causes destructive cracking, one of several different oxides may be added to stabilize zirconia. This eliminates, or at least reduces, the effects of the transformation from monoclinic to tetragonal zirconia. In commercial usage,

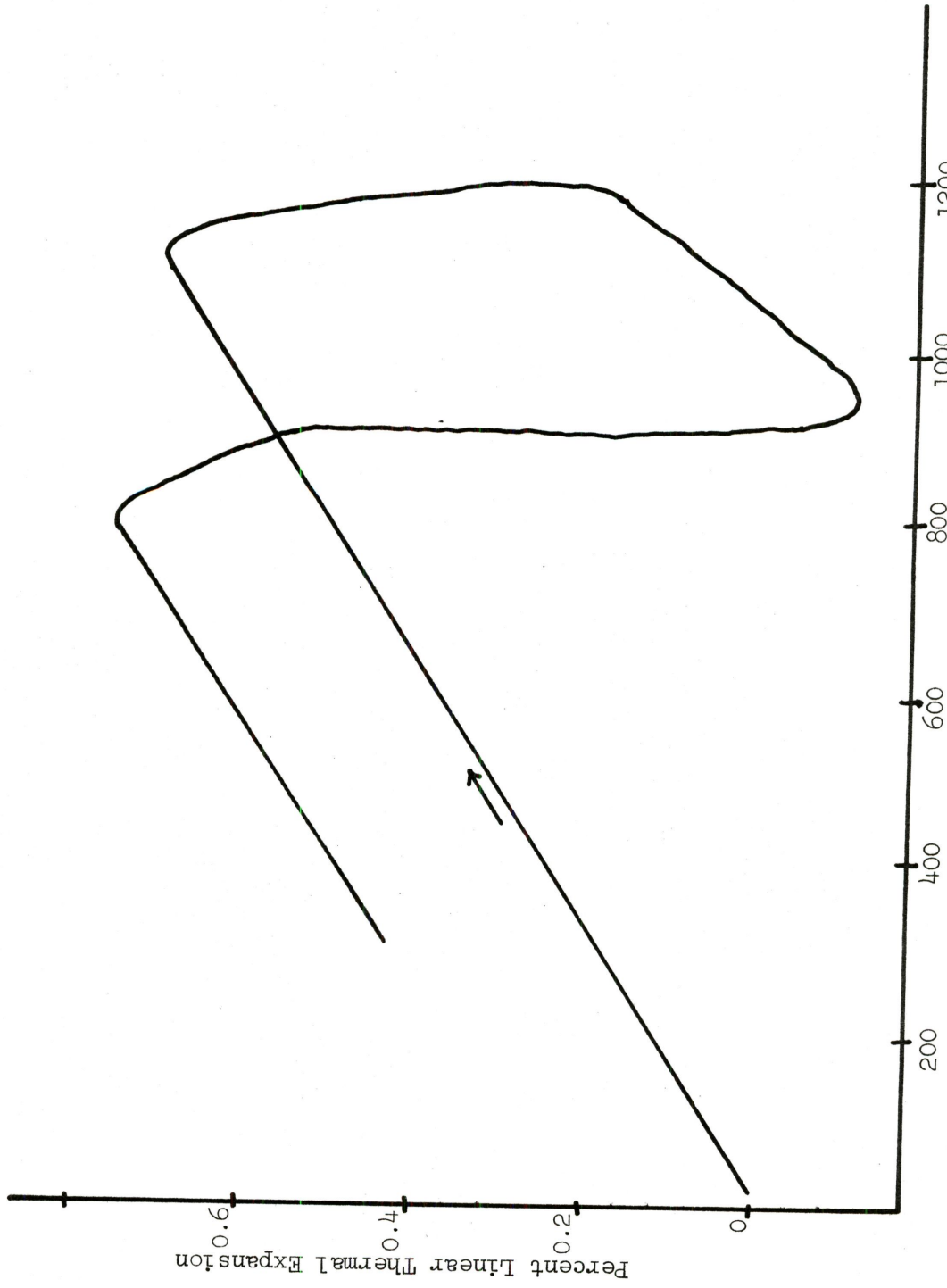


Figure 2. Linear Thermal Expansion of Monoclinic Zirconia[8]

the addition of calcia is most common. If between 16 and 29 mole percent of calcia is added to zirconia, the zirconia forms a cubic solid solution which is stable to room temperature. With the addition of less than 16 percent calcia the zirconia is called partially stabilized, i.e., there is some cubic solid solution but also some monoclinic phase in equilibrium; thus the monoclinic to tetragonal transformation can still be seen, but depending on the percentage of calcia, it is less destructive. The melting point is lowered by calcia additions, as shown in the phase diagram, Figure 3.

The stability of calcia stabilized zirconia is excellent. Isothermal tests[9] at 1375 °C for 336 hours, 1200 °C for 520 hours, 1100 °C for 812 hours, 980 °C for 1473 hours, and 815 °C for 2011 hours showed that there was no loss in stabilization, i.e., no decrease in the amount of cubic zirconia, with long term firing.

Duwez[9] found from differential thermal analysis that the transformation temperature from tetragonal to monoclinic zirconia was lowered as the amount of calcia (up to 16 mole percent) was increased, as shown in Figure 4. This transformation temperature depression was also found in the zirconia-magnesia and zirconia-ceria systems.

Lattice parameter variations as the amount of calcia was changed were also determined by Duwez, Figure 5. For his work the samples were fired at 2000 °C. Lattice parameters were determined from high angle reflections only and a 143.2 mm camera was used for diffraction analysis.

Garvie[10] criticized the phase diagram of Duwez and determined a much smaller region of cubic solid solution. He tentatively determined a second CZ compound, $CaZr_4O_9$, which exists in an alpha form from 1240 °C

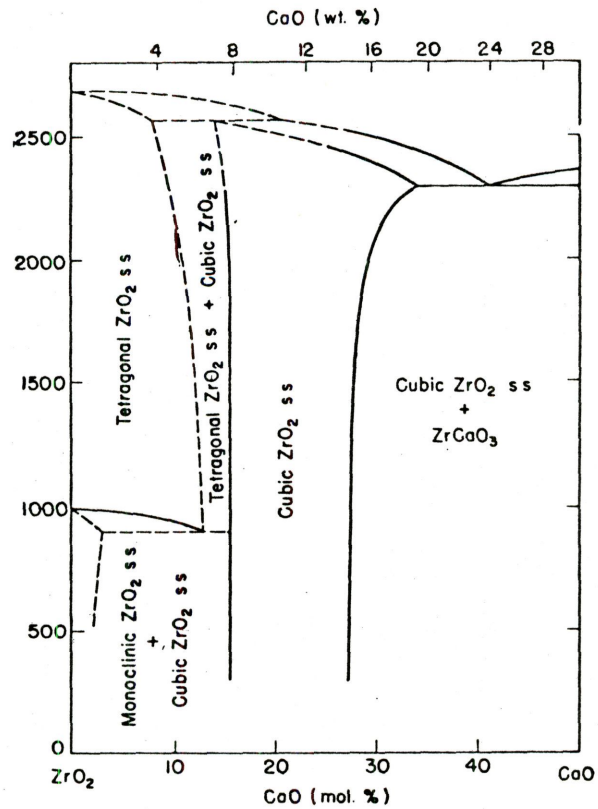


Figure 3. Phase Diagram of the $CaO-ZrO_2$ System as Determined by Duwez[9]

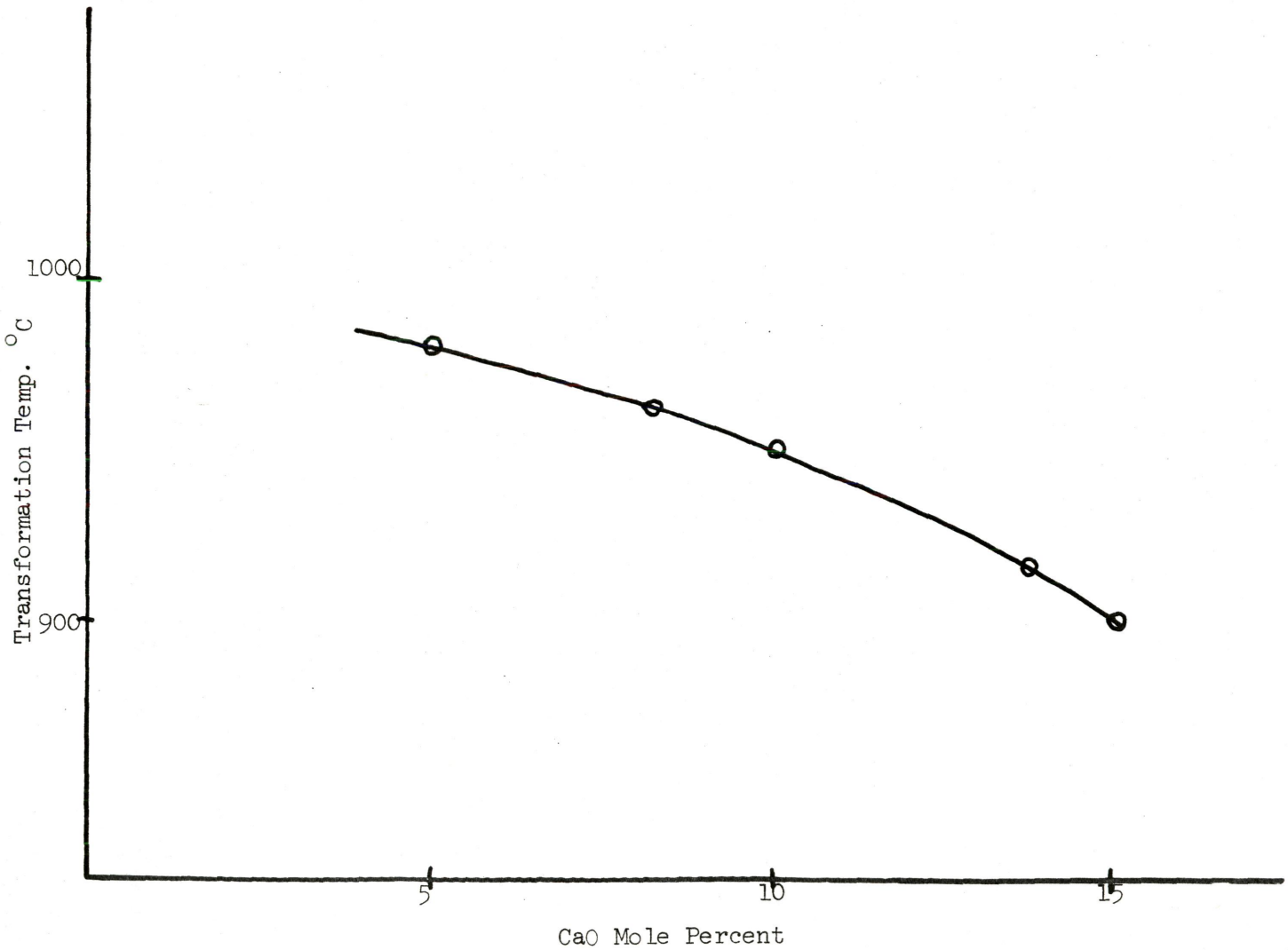


Figure 4. Effect of the Amount of Calcia on Transformation Temperature from Cubic to Monoclinic Zirconia[9]

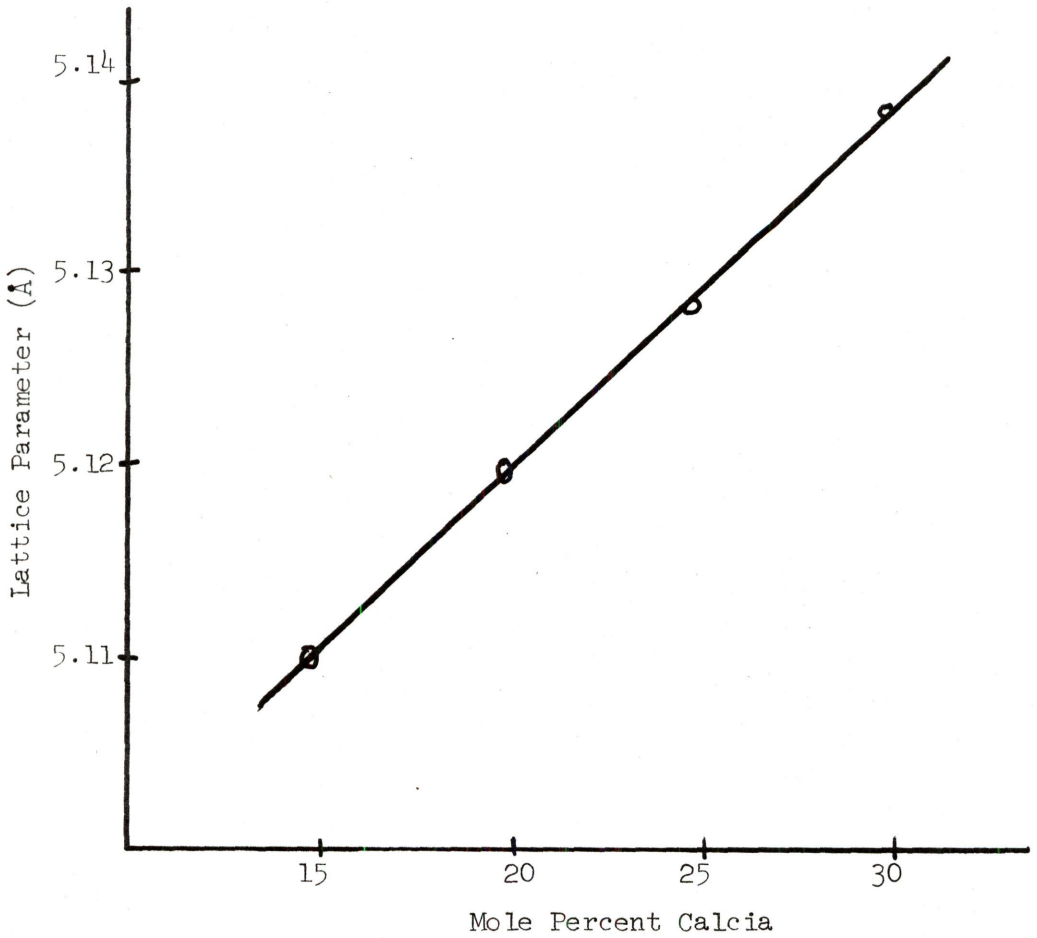


Figure 5. Lattice Parameter Variations with Solid Solution Changes in Cubic Zirconia[9]

to 1650 °C and above 1650 °C exists in a beta form. If the cubic phase is metastable, as he asserted from the work of Weber[11], then there is great difficulty in determining the actual equilibrium phases. Garvie used lattice parameter determinations employing the Nelson-Riley extrapolation and a Debye-Scherrer camera of 114.6 mm diameter to determine changes in the structure of the solid solution. Figure 6 shows his lattice parameter determinations and the resulting phase diagram, both of which differ considerably from the information published by Duwez[9].

Garvie discovered that the raw materials used may cause variations in the cubic solid solution. He showed that the use of $CaCO_3$ as a reagent resulted in a larger cubic field than the use of CaO. He theorized that with $CaCO_3$ as a reagent, as the salt decomposed, an active intermediate oxide formed which caused an irreversible, metastable formation of the cubic phase. This problem may also partially explain the discrepancies in different phase diagram information that has been published for the system. Garvie also stated that the strain energy involved in the transformation from tetragonal to monoclinic zirconia must be considered an additional degree of freedom. Such an explanation is necessary in order to draw the cubic boundaries as he did at 1200 °C and not violate the Gibbs Phase Rule.

Gavrish[12] has also studied the stability of calcia stabilized zirconia. His work indicated that the temperature of maximum destabilization is approximately 1400 °C. This, he determined, is also true for yttria stabilization, but for magnesia stabilization the temperature of maximum destabilization is only 1200 °C. He determined that yttria stabilized zirconia has the greatest stability and at the lowest mole

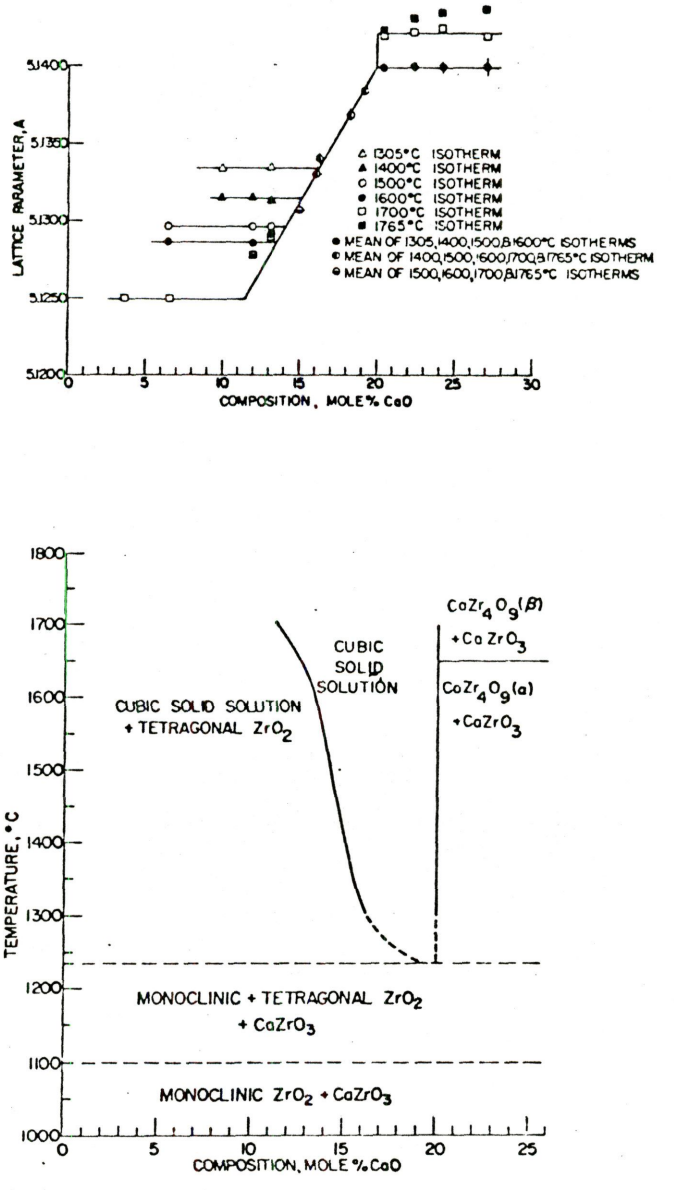


Figure 6. Phase Diagram and Lattice Parameter Data for the $CaO-ZrO_2$ System after Garvie[10]

percent of the three additives, Table 2. Note that his studies extended only 60 hours. For raw materials he used a 99.7% pure zirconia and $CaZrO_3$ which had been prepared from zirconia and calcium carbonate. Firing temperature was 1750 °C for five hours and the samples were quenched. Phase analysis was by quantitative X-ray diffraction determination. Gavrish theorized that the reason for varying stability of different oxides is related to the size of the different ions, i.e., magnesium is the smallest and yttrium is the largest. The substitution of a small ion into the zirconia lattice increases the stresses more than the substitution of a larger ion more nearly the size of the zirconium ion. The activation energy of the diffusion process is thus decreased and the rate of decomposition is increased. Table 3 lists accepted values for various ionic radii.

Table 3. Ionic Crystal Radii[13]

Ion	Al^{3+}	Mg^{2+}	Zr^{4+}	Y^{3+}	Ce^{4+}	Ca^{2+}
Radius (A)	0.51	0.67	0.79	0.92	0.94	0.99

Gavrish also studied the stability of cubic zirconia heated in argon. With calcia and yttria stabilization he found no change in results from those samples heated in air. With magnesia he found that the lattice parameters changed, indicating a change in the structure of the solid solution. It indicated that some of the magnesia was vaporizing from the solid solution. At 2300 °C the cubic structure remained only with a composition of 12 mole percent magnesia and the X-ray pattern indicated that there was considerable stress in the structure. The same

Table 2. Decomposition of the Solid Solutions during Heating in Air

Concentration of the oxide additive in mole %		Destabilization at 1200 °C for 60 h.		Destabilization at 1400 °C for 60 h		Destabilization at 1600 °C for 60 h	
		Cubic ZrO_2, in %	Monoclinic ZrO_2 in %	Cubic ZrO_2, in %	Monoclinic ZrO_2 in %	Cubic ZrO_2, in %	Monoclinic ZrO_2 in %
CaO	6	85	15	74	25	93	7
	12	100	0	98	2	100	0
	15	100	0	100	0	100	0
	20	100	0	100	0	100	0
MgO	12	20	80	45	55	100	0
	15	0	100	20	80	100	0
	20	0	100	10	90	100	0
Y_2O_3	8	98	2	88	12	91	9
	12	100	0	100	0	100	0
	15	100	0	100	0	100	0

samples were thermally cycled from 2000 °C and 2300 °C to room temperature to study destabilization. As in the other experiments, calcia and yttria stabilization proved to be completely stable but the magnesia stabilization was lost, particularly at 2300 °C, in a short period of time.

Magnesia has been used commercially to stabilize zirconia. However, at equilibrium the cubic solid solution was found not to exist below approximately 1375 °C. Thus, although magnesia stabilized zirconia may be prepared, it reverts to its unstabilized form with time above 1000 °C. Therefore, magnesia stabilization is not generally as useful as calcia stabilization.

The stabilization of zirconia by several other oxides has been studied.[8, 12] Many of the rare earths have been used, although on a commercial basis the cost is usually too high. Yttria and ceria are two oxides that may be used successfully. With ceria a different mechanism of stabilization is found. With the addition of greater than 15 mole percent ceria to zirconia the temperature of the monoclinic to tetragonal transformation is lowered below room temperature. There is still a cubic solid solution structure above 1000 °C to 2000 °C, depending on the composition, but it is not relevant to the stabilization problem, since the destructive transformation does not appear in normal usage.

$CaO\text{-}Al_2O_3$

The calcia-alumina binary has had much investigation. However, there has been considerable discrepancy about the actual phases that exist at equilibrium. Of particular importance to this study is the compound originally called C_3A_5 and more recently determined to be CA_2. It

is apparent that earlier researchers obtained the same compound but incorrectly determined the stoichiometry. The calcium aluminates are of primary importance to the study of cements and therefore much work has been done with the various hydrated forms. This is generally not relevant to the calcia-alumina-zirconia ternary system.

As determined by Nurse, et.al.,[14] there are four binary compounds in the $CaO-Al_2O_3$ system: C_3A, CA, CA_2, and CA_6. Lea and Desch[15] add $C_{12}A_7$, which Nurse stated is not an anhydrous compound and thus not properly part of the binary system. Nurse determined that thermdynamically a mixture of CA and C_3A is more stable than $C_{12}A_7$ up to the melting point of $C_{12}A_7$, which is 1392 °C. He was not able to prepare completely anhydrous $C_{12}A_7$ and found that the formula is most accurately, at 950 °C, $C_{12}A_7 \cdot H_2O$. Thus it is most probable that $C_{12}A_7$ is metastable. C_5A_3 has also been suggested, possibly as a polymorph of $C_{12}A_7$. Nurse says that it is metastable. Berezhnoi[1] did show C_5A_3 in his ternary diagram. Brooksbank[16] also considered $C_{12}A_7$ to be a part of the binary system. CA_6 has also been called C_3A_{16} as published by the American Ceramic Society[17], but generally it has been accepted to have the formula CA_6. Figure 7 shows the complete phase diagram as determined by Lea and Desch.[15]

Nurse showed that the four calcium aluminates, C_3A, CA, CA_2 and CA_6, melt incongruently, although CA and CA_2 are only very slightly incongruent. If CA_2 were considered to be C_3A_5, then it would have to be shown as a congruently melting compound.

An examination of X-ray data published by JCPDS[18] shows that CA_2

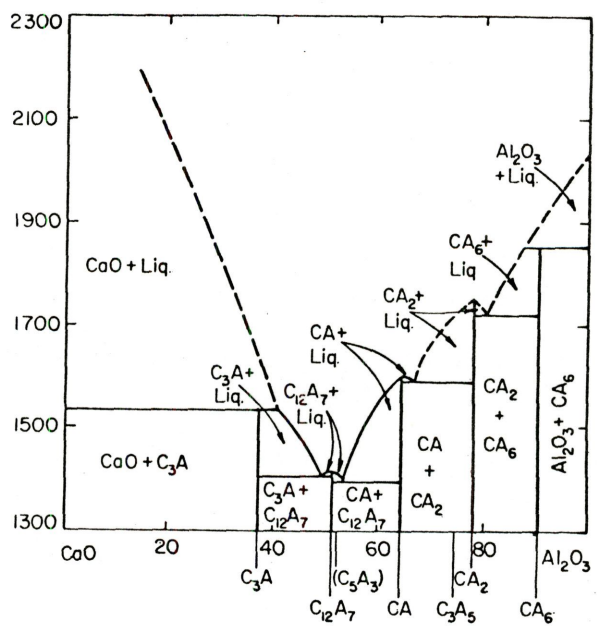


Figure 7. Phase Diagram of the CaO-Al_2O_3 System as determined by Lea and Desch [15]

and C_3A_5 have been listed with almost identical patterns. This could be understood if one accepted that the real compound is either one or the other, and the remaining stoichiometric formulation is really a solid solution. Brooksbank showed that the linear coefficient of thermal expansion is approximately the same, as determined by authors who claimed to have C_3A_5 and as he determined for what he called CA_2. His value for thermal expansion was $5.0 \times 10^{-6}/^{\circ}C$ from 0 °C to 800 °C. Rigby and Green[19] determined a value of $3.5 \times 10^{-6}/^{\circ}C$ from 100 °C to 800 °C. They attempted to prepare CA_2 from a stoichiometric mixture, but after heating to 1530 °C they found the resultant mixture to be C_3A_5 and free alumina, from an optical thin section examination. In their observation CA is the most easily prepared of the calcium aluminates and it is for that reason, they explained, that one could obtain excess CA when starting from a CA_2 stoichiometry. They stated very strongly that the equilibrium state is C_3A_5.

Goldsmith[20] prepared samples from the melt and found that when CA_2 stoichiometry was used as the starting mixture, that he saw optically only a single phase. When C_3A_5 stoichiometry was used, he saw two phases. Firing was done at 1500 °C. Goldsmith's work was done to confirm earlier work of Tavisci[21] and came to similar conclusions. Wisnyi[22] did considerable work studying CA_2 and it is his X-ray information that is published by JCPDS. Wisnyi determined that the density of CA_2 is 2.86 g/cc. Table 4 shows a comparison between the results of X-ray indexing obtained by Wisnyi and later research done by Baldock.[23] There are no significant disagreements, but enough minor discrepancies to question if the structure

Table 4. Powder Diffraction Data for $CaO \cdot 2Al_2O_3$ [23]

WISNYI	(ASTM 7-0032)	PRESENT WORK			
d	I/I_{100}	h k l	d_{obs}	d_{calc}	I/I_{100}
		1 1 0	7.196	7.2091	½B
6.193	20	2 0 0	6.161	6.1642	7
		1 1 -1	4.607	4.6101	3
4.439	75	0 2 0	4.4416	4.4437	54
		1 1 1	3.913	3.9164	1
		3 1 0	3.727	3.7302	½
3.609	20	2 2 0	3.604	3.6048	20
3.520	100	3 1 -1	3.503	3.5020	100
3.372	5	0 2 1	3.379	3.3801	2
3.239	20	2 2 -1	3.234	3.2326	7
3.079	55	4 0 0	3.0840	3.0823	29
2.882	50	1 3 0	2.882	2.8806	20
2.760	60	2 2 1	2.753	2.7526	27
2.717	55	3 1 1	2.712	2.7120	23
		0 0 2		2.6033	
2.607	85	1 1 -2	2.5989	2.5939	60
		1 3 -1		2.5965	
2.531	25	4 2 0	2.534	2.5327	13
		3 1 -2	2.462	2.4621	4
		1 3 1	2.452	2.4509	3
2.436	35	5 1 -1	2.436	2.4351	17
		3 3 0	2.404	2.4032	3
		4 0 -2	2.350	2.3556	½B
2.350	35	1 1 2	3.325	2.3255	10
		0 4 0	2.222	2.2219	1
2.208	40	2 0 2	2.181	2.1815	7
		2 4 0	2.0887	2.0903	2
		4 2 1		2.0894	
		4 2 -2	2.0827	2.0813	2
		5 1 -2	2.0678	2.0676	6
		6 0 0	2.0539	2.0549	14
2.059	55	3 3 1		2.0531	
		0 4 1	2.044	2.0437	4
		2 4 -1	2.0095	2.0097	2
2.003	40	1 3 -2	2.0001	2.0004	7
		5 1 1	1.9634	1.9636	5
1.960	25	2 2 2	1.9592	1.9583	5
1.941	30	3 3 -2	1.9379	1.9381	3
		6 2 -1	1.9251	1.9248	1
		5 3 -1			
1.904	25	6 0 -2	1.9049	1.9052	7
		5 3 0	1.8956	1.8953	5
1.875	40	1 3 2	1.8683	1.8693	5
1.801	30	4 4 -1	1.8007	1.8007	11
1.760	20	3 1 -3	1.7615	1.7619	10
		6 2 -2	1.7502	1.7511	½
		7 1 0	1.7277	1.7277	½
		5 3 -2		1.7272	

WISNYI	(ASTM 7-0032)	PRESENT WORK			
d	I/I_{100}	h k l	d_{obs}	d_{calc}	I/I_{100}
		2 4 -2	1.7140	1.7147	½
		1 5 -1	1.6880	1.6882	5
		7 1 -2	1.6780	1.6771	½
		5 3 1	1.6646	1.6652	1
		1 5 1	1.6461	1.6462	½
		5 1 -3	1.6372	1.6374	1
		4 2 2	1.6306	1.6309	4
1.628	30	6 2 1	1.6247	1.6249	5B
		4 2 -3		1.6244	
		4 4 1	1.6204	1.6202	6
		3 5 -1	1.6112	1.6109	2
		7 3 -1	1.5623	1.5624	2B
1.556	20	2 4 2	1.5570	1.5567	3
		5 1 2	1.5523	1.5516	5
		8 0 0	1.5405	1.5412	5
		6 4 -1		1.5397	
1.537	30	3 3 -3	1.5364	1.5368	12
		1 3 -3	1.5334	1.5335	12
		7 1 1		1.5155	
1.511	25	8 2 -1	1.5145	1.5146	4
		7 3 0		1.5140	
		6 4 0	1.5091	1.5087	1
1.475	5	0 6 0	1.4808	1.4813	4
		6 2 -3		1.4807	
		2 2 3	1.4691	1.4692	1
		3 5 -2	1.4603	1.4606	1
		8 2 0	1.4561	1.4561	1
		8 2 -2	1.4521	1.4524	2
		5 3 -3		1.4521	
		1 3 3	1.4445	1.4439	½
		2 6 0	1.4401	1.4403	2
		1 5 2	1.4305	1.4304	1
		0 6 1	1.4248	1.4248	2
		9 1 -1	1.4133	1.4132	½
		2 6 -1		1.4131	
1.403	5	2 4 -3	1.4054	1.4054	2
1.372	45	6 4 1	1.3729	1.3727	9B
		4 4 -3		1.3725	
		7 3 1	1.3648	1.3651	1
		2 6 1		1.3646	
		2 0 -4	1.3560	1.3560	1
		6 2 2			
		9 1 0	1.3539	1.3540	2
		4 0 -4	1.3479	1.3482	½
1.337	25	4 6 0	1.3350	1.3352	5
1.319	20				

of CA_2 is fixed. In preparing CA_2 with a CA impurity of only 0.5 weight percent Baldock used dried analar calcite and gibbsite mixed stoichiometrically and fired for five hours at 1400 °C to 1450 °C. He used a Phillips diffractometer for X-ray analysis, whereas Wisnyi used a powder camera.

No one has suggested that both CA_2 and C_3A_5 exist in equilibrium or that the structure exists as a solid solution. Since the published X-ray patterns are similar, perhaps this possibility should be considered. The possibility of hydrated products should also be considered, since in other calcium aluminates, hydrates are important phases. The preparation of pure samples is apparently a problem which may also hinder an accurate understanding of the structure and properties of CA_2.

Al_2O_3-ZrO_2

The Al_2O_3-ZrO_2 binary system has no compounds. If Dietzel's rules concerning cation field strength are considered, this is to be expected. By Dietzel's calculations[24] the field strength of Al is 0.96 and that of Zr is 0.77. Since the difference is only 0.19, less than the 0.3 difference required for compound formation, it is predicted that no stable compound can be formed between the oxides of zirconium and aluminum.

Hennicke[25] found that alumina can be used to partially stabilize zirconia. He mixed $Zr(OH)_4$ and $Al(OH)_3$ together and fired at temperatures from 1200 °C to 1600 °C. He also experimented with oxide powders sintered at 1600 °C. Approximately one mole percent of alumina entered the zirconia lattice. This solution caused part of the zirconia to remain in the tetragonal form at room temperature. After several of his samples

were ground, they contained more monoclinic zirconia than before grinding, which indicated that there was also a mechanical stabilization. Of practical importance was his discovery that on repeated thermal cycling, mixtures of more than ten mole percent Al_2O_3 became brittle. Another important observation was that the corundum structure absorbed part of the stress that was caused by the density change when the transition from tetragonal to monoclinic zirconia occurred. Hennicke also observed that the temperature at which the tetragonal to monoclinic transition occurred was lowered as the percentage of alumina was increased, when a cooling rate of 10 $^{\circ}C$ per minute was maintained.

The Disappearing Phase Method of Phase Diagram Determination

The disappearing phase method[26] uses quantitative X-ray diffraction analysis to determine phase boundaries on a phase diagram. Several samples of differing phase compositions are analyzed by X-ray diffraction and a weight ratio or a mole ratio of two phases for each composition is determined. The relationship between weight ratio or mole ratio of two phases and the phase composition is linear so that an extrapolation may be made to determine at what composition the phase ratio becomes zero. This determines the position of the phase boundary. The method can be used in a ternary system if the amount of one component is held constant and the variation of the remaining two components is observed. For solid solution endpoints which vary in composition with temperature, the composition at constant temperatures may be evaluated by this technique.

CHAPTER III

PROCEDURE

Forty-six samples were prepared with a minimum of 55 mole percent zirconia for determining the phase diagram of the high zirconia region of the calcia-alumina-zirconia ternary system. Using quantitative and qualitative phase analysis and lattice parameter information determined from X-ray diffraction, the phase diagram was determined by the disappearing phase technique. The raw materials used were TAM CP zirconia of greater than 99.0% purity and 1.4 micron particle size, Alcoa A-16 Superground alumina, and Fisher Scientific Certified calcium carbonate, 99.9% pure. Optical analysis was made with a metallographic microscope to confirm the X-ray results. Three compositions were chosen to be fired for up to 2000 hours to determine stability of the phases. X-ray analysis was used to determine the phase stability.

Sample Preparation

Compositions for four separate series of firings were chosen in the high zirconia region of the ternary system. Tables 5, 6, 7, and 8 show the compositions which were chosen for the four series of samples. For series 1, series 2, and series 4, all three components were weighed out for each composition and each was mixed thoroughly in an alumina automatic mortar and pestle for 30 minutes in acetone. Several pellets of each composition were pressed using a Carver hydraulic laboratory press to 5000 psi. in a stainless steel die 0.75 inches in diameter lubricated

Table 5. Composition of Series 1

Sample Number	ZrO_2 mole %	Al_2O_3 mole %	CaO mole %
1-1	64.0	20.0	16.0
1-2	68.0	20.0	12.0
1-3	72.0	20.0	8.0
1-4	69.6	13.0	17.4
1-5	74.0	13.0	13.0
1-6	78.3	13.0	8.7
1-7	76.2	4.8	19.0
1-8	80.9	4.8	14.3
1-9	85.7	4.8	9.5

Table 6. Composition of Series 2

Sample Number	ZrO_2 mole %	Al_2O_3 mole %	CaO mole %
2-1	55.0	25.0	20.0
2-2	57.5	25.0	17.5
2-3	60.0	25.0	15.0
2-4	62.5	25.0	12.5
2-5	65.0	25.0	10.0
2-6	60.0	20.0	20.0
2-7	62.5	20.0	17.5
2-8	65.0	20.0	15.0
2-9	67.5	20.0	12.5
2-10	70.0	20.0	10.0
2-11	65.0	15.0	20.0
2-12	67.5	15.0	17.5
2-13	70.0	15.0	15.0
2-14	72.5	15.0	12.5
2-15	75.0	15.0	10.0
2-16	70.0	10.0	20.0
2-17	72.5	10.0	17.5
2-18	75.0	10.0	15.0
2-19	77.5	10.0	12.5
2-20	80.0	10.0	10.0
2-21	75.0	5.0	20.0
2-22	77.5	5.0	17.5
2-23	80.0	5.0	15.0
2-24	82.5	5.0	12.5
2-25	85.0	5.0	10.0

Table 7. Composition of Series 3

Sample Number	ZrO_2 mole %	Al_2O_3 mole %	CaO mole %
3-1	64.0	20.0	16.0
3-2	68.0	20.0	12.0
3-3	72.0	20.0	8.0
3-4	69.6	13.0	17.4
3-5	74.0	13.0	13.0
3-6	78.3	13.0	8.7
3-7	76.2	4.8	19.0
3-8	80.9	4.8	14.3
3-9	85.7	4.8	9.5
3-10	80.0	0	20.0
3-11	85.0	0	15.0
3-12	90.0	0	10.0

Table 8. Composition of Series 4

Sample Number	ZrO_2 mole %	Al_2O_3 mole %	CaO mole %
4-1	22.0	33.0	45.0
4-2	40.0	20.0	40.0
4-3	50.0	12.0	38.0
4-4	60.0	12.0	28.0

with stearic acid in acetone. No binder was found to be required since the pellets held together and no laminations appeared. The thickness of the pellets was approximately 0.25 inches.

Series 1 pellets were calcined at 1200 °C in a silicon carbide resistance furnace for 3.5 hours and fired to 1700 °C in a gas fired furnace for three hours. The pellets were allowed to slow cool in the furnace before being removed.

Series 2 and series 4 samples were calcined as powders at 1300 °C for 16 hours. The calcined powders were remixed in the automatic mortar and pestle and pressed as pellets. The pellets were sintered at 1500 °C in a silicon carbide resistance furnace for 20 hours. Cooling was controlled at a rate of one degree per minute. After the series 2 samples had been analyzed as described below, they were all reloaded into the furnace and refired to 1500 °C for 20 hours. After 20 hours at 1500 °C they were rapidly removed and quenched in water.

For series 3 a different method of preparation was used. The correct proportions of calcia and zirconia were mixed in the automatic mortar and pestle for one hour. These mixtures were calcined as powders at 1400 °C for 16 hours. After this stabilized zirconia was prepared, alumina of the required proportions was added, mixed, and the powder pressed into pellets as described above. These pellets were fired at 1500 °C for 25 hours and slow cooled at one degree per minute.

For the determination of the long term phase stability, three compositions were chosen as shown in Table 9. Four kilograms of each composition was prepared. Each batch was mixed in a polyethylene jar with

alumina balls for 24 hours and the powder was calcined at 1200 °C for 20 hours. The calcined powder was examined by X-ray diffraction to determine if a stable ratio of cubic to monoclinic zirconia had been achieved. The batches were reground in the polyethylene jars and recalcined twice before a constant cubic to monoclinic zirconia ratio was obtained. One hundred pellets of each composition were prepared and fired to 1550 °C for 24 hours. Fifty were placed in an electric resistance furnace and brought up to 900 °C and 50 were placed in a second furnace and brought up to 1300 °C. All of the pellets were placed on stabilized zirconia plates which were stacked for maximum use of the furnace space. At 200 hours two pellets of each composition at each temperature were removed. The furnace door was opened and the required pellets removed as quickly as possible and thus air cooled, without affecting the remaining pellets. This procedure was followed successively at each 200 hours up to 2000 hours. At 1000 hours both furnaces were cooled to room temperature at one degree per minute to examine the contents and to remove other samples not involved with the phase stability work. Both furnaces were reheated at the same one degree per minute to 900 °C and 1300 °C respectively for the second one thousand hours.

Table 9. Composition of Batches for Long Term Firing

Batch Designation	ZrO_2 mole %	Al_2O_3 mole %	CaO mole %
A	77.5	10.0	12.5
B	68.0	17.5	14.5
C	57.5	25.0	17.5

Qualitative X-Ray Analysis

For all of the X-ray work a Philips Electronics diffractometer with a solid state scintilation detector and Ortec single channel amplifier, rate meter, and associated electronics with output displayed on a Bristol ten millivolt recorder was used. This unit employed nickel filtered Cu $K\alpha$ radiation and the X-ray tube was operated at 45 kv and 25 ma. Geometrically the X-ray beam had a 4° take off angle, a 1° divergence slit, a 1° scatter slit, and a 0.003 inch receiving slit. All scans were run at one degree per minute unless otherwise noted. Powder samples were back loaded into an aluminum holder and packed onto a frosted glass slide to give a random surface for scanning. For identification of phases, scans were made from $2\theta = 14^{\circ}$ to $2\theta = 70^{\circ}$. Comparison was made to the Joint Committee on Powder Diffraction Standards Powder Diffraction File to determine exactly which phases were present as each line in the X-ray scan was accounted for.

One pellet of each of the series 1 compositions was crushed and ground to approximately -325 mesh in the automatic mortar and pestle for X-ray analysis. For the remaining series of samples it was determined that X-raying the surface of the pellets was satisfactory and less time consuming than crushing the pellets, which were very difficult to grind. The surface of each pellet was ground slightly with silicon carbide paper of 180 and 320 grit to insure a flat surface which would fit reproducibly into the sample holder clip of the goniometer.

Quantitative X-Ray Analysis

Azaroff[27] showed that for polymorphic modifications of the same

composition (such as cubic zirconia and monoclinic zirconia) the weight ratio of the two polymorphs in a mixture is directly proportional to the ratio of the two peak heights, one generated by each crystalline structure. He recommended preparing a graph to relate intensity ratios to composition. In order to follow this procedure, samples of pure cubic zirconia (15 mole percent CaO) and of pure monoclinic zirconia were mixed together in the automatic mortar and pestle to have weight ratios (cubic: monoclinic) of 4:1, 1:1, and 1:4. An X-ray scan was made of each composition from $2\theta = 27^{\circ}$ to $2\theta = 32^{\circ}$. For the cubic phase the major peak of 100% intensity corresponding to the 111 plane at a d spacing of 2.92 A was chosen. Two peaks from the monoclinic phase were chosen to compare to the cubic peak in order that two separate weight ratios might be determined. The values reported are an average of the two weight ratios. Both monoclinic peaks were close to the cubic peak: one corresponded to the $11\bar{1}$ plane at d spacing 3.16 A and the other to the 111 plane at d spacing 2.834 A. Ratios of peak intensity for the three standard samples were determined and a graph was constructed to be used for determining weight ratios for all of the samples, Figure 8. The equations for the two lines are as follows:

$$Y_1 = 2.027\ X_1 + 0.054 \qquad Y_2 = 3.082\ X_1 + 0.105 \qquad (1)$$

where Y_1 is $\dfrac{\text{intensity of cubic 111 peak}}{\text{intensity of mono 111 peak}}$

X_1 is $\dfrac{\text{weight cubic}}{\text{weight mono}}$

Y_2 is $\dfrac{\text{intensity of cubic 111 peak}}{\text{intensity of mono } 11\bar{1} \text{ peak}}$.

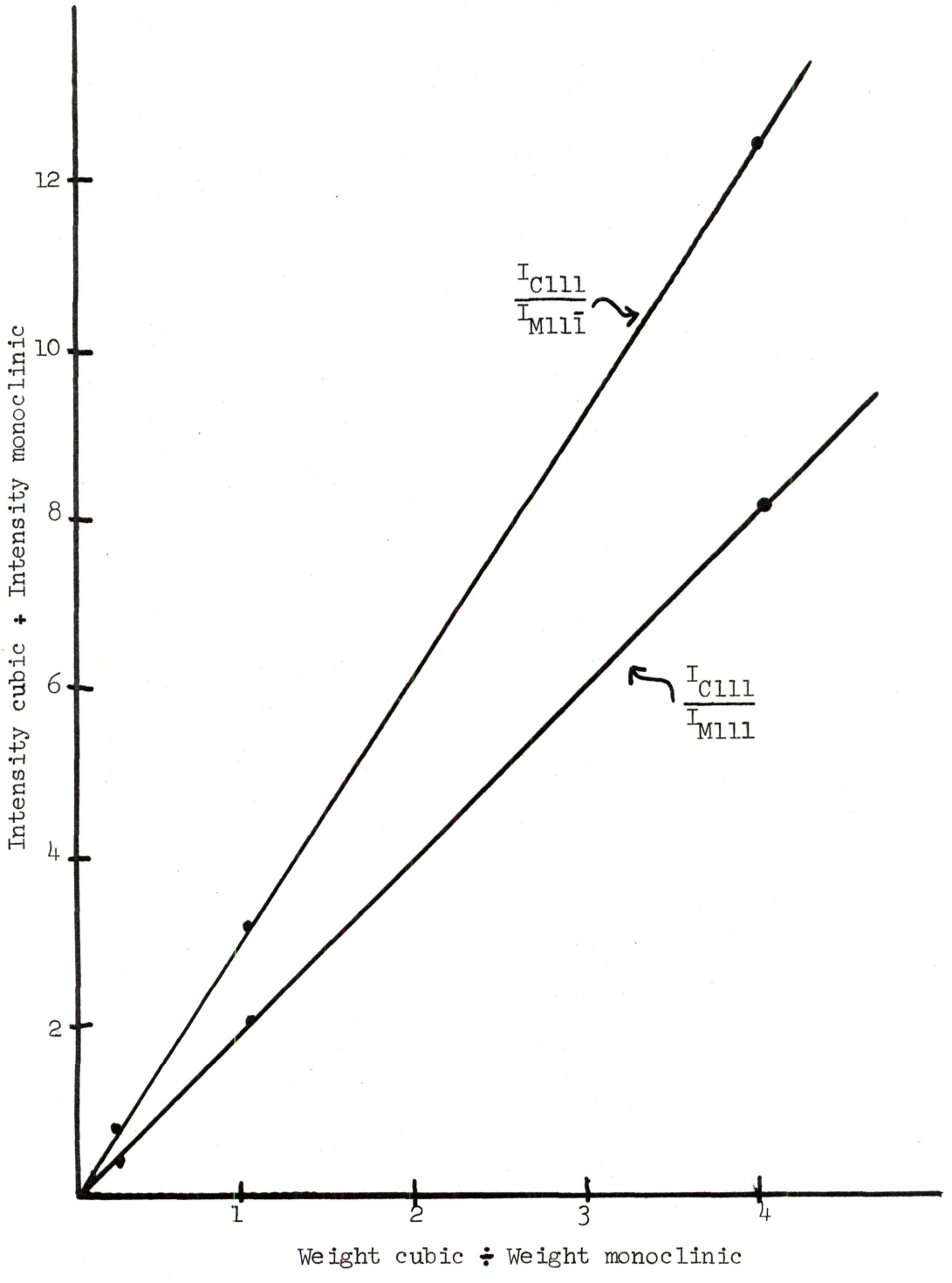


Figure 8. Relationship between Peak Intensities and Weight Ratios of Cubic to Monoclinic Zirconia

For each of the samples which had both cubic zirconia and monoclinic zirconia, a determination of the weight ratio was made from these equations. The average value determined from the two ratios was calculated.

Lattice Parameter Measurement

Lattice parameter values were determined for the cubic zirconia phase in samples A, B, and C at 0, 200, 1000, and 2000 hours at 900 °C and 1300 °C, and also at 400 hours for the 1300 °C samples. X-ray scans were made at one half degree per minute from $2\theta = 13^{\circ}$ to $2\theta = 135^{\circ}$. From information in the JCPDS files relating to d spacing in crystalline planes accurate values for the a parameter were determined by using the following formula:

$$\frac{1}{d^2} = \frac{h^2}{a^2} + \frac{k^2}{a^2} + \frac{l^2}{a^2} \qquad (2)$$

where h, k, l are the indices of the plane

a is the lattice parameter (in a cubic structure all three dimensions are the same)

d is the interplanar spacing.

Bragg's Law gives the relationship between d and θ, the angle of diffraction in terms of λ, the wavelength of radiation used, in this case 1.5418 A for Cu Kα:

$$n\lambda = 2d \sin\theta \qquad (3)$$

where n is an integer.

In order to determine the actual lattice parameter a for any particular sample, an extrapolation must be made. For this a was plotted versus $\cos\theta\cot\theta$ and this curve was extrapolated to the point where

$\cos\theta\cot\theta$ is zero. This value of $\underline{a}$ at $\cos\theta\cot\theta = 0$ is the true lattice parameter for the sample. For actually determining this intercept a PDP 8 computer which had been programmed to do a least squares regression was used to give an accurate estimate of the lattice parameter. The program also gave a value for the correlation coefficient of the estimate, an indication of the closeness of all of the points to the line. Figure 9 gives an example of one extrapolation that was made.

An attempt at extrapolation by relating $\underline{a}$ to $\cos^2\theta$ was also made, but this was not accurate compared to the extrapolation of the $\underline{a}$ versus $\cos\theta\cot\theta$ graph. Generally the $\underline{a}$ versus $\cos\theta\cot\theta$ extrapolation works better than the $\underline{a}$ versus $\cos^2\theta$ extrapolation when the X-ray beam is aligned so that it is not exactly aimed at the plane of the surface of the sample. This misalignment does not particularly affect the accuracy of lattice parameter determinations when the $\cos\theta\cot\theta$ extrapolation is used.

Quantitative Optical Determination

One pellet of each sample was prepared for optical examination by mounting in Quickmount, a self-setting resin type of translucent plastic commonly used for metallographic work. Each pellet was wet polished successively on 180, 320, and 600 grit silicon carbide grinding paper. Final polishing was done with a Syntron automatic vibrating polisher. One micron diamond paste with water as a lubricant was used on a nylon cloth surface. Twenty-four hours of polishing on this device was required to obtain a satisfactory surface on each sample. Each sample was

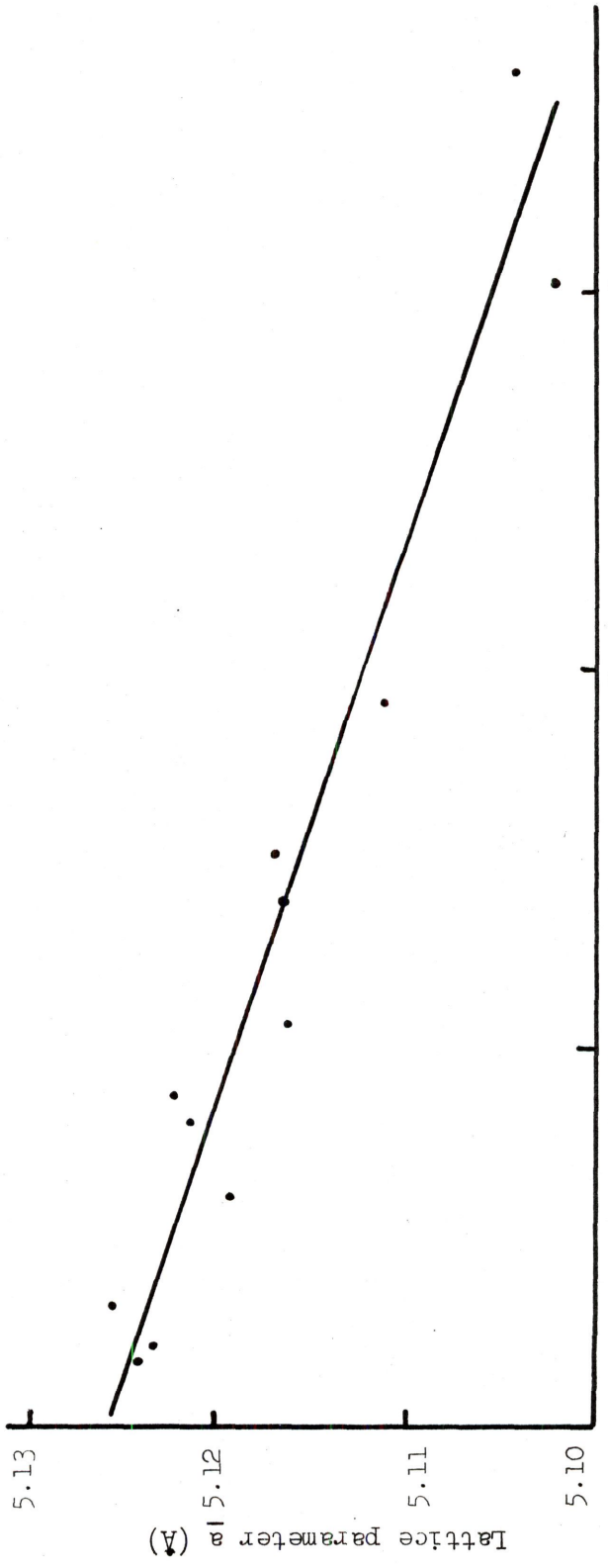


Figure 9. Lattice Parameter Extrapolation for Composition A before Heat Treatment

photographed using a Polaroid attachment on a Reichert Metallographic Microscope at 600x in reflected light and bright field. From these photographs the volume fraction of each phase was determined by a systematic point counting technique, which is described in Appendix A.

Density Determination

The bulk density of each sample was determined by a technique involving immersion in kerosene. Each sample was weighed on an accurate balance. For 24 hours all of the samples were soaked in kerosene in order to fill all of the pores. After soaking, each sample was weighed again while suspended on a wire mesh hanger in a beaker of kerosene, insuring that no air bubbles remained attached to the pellet. Density was calculated from the following formula:

$$\text{density} = \frac{\text{d.w.}}{\text{d.w.} - \text{s.w.}} \times \text{s.g.} \qquad (4)$$

where d.w. is the dry weight

s.w. is the suspended weight

s.g. is the specific gravity of the kerosene.

CHAPTER IV

RESULTS AND DISCUSSION OF RESULTS

From qualitative and quantitative X-ray analysis of fired samples, a phase diagram was determined for the zirconia rich corner of the CaO-Al_2O_3-ZrO_2 ternary system. Comparison of the analysis of samples fired at 1500 °C for 20 hours and for an additional 20 hours was made to prove that the derived diagram was indeed an equilibrium diagram. From optical analysis of the samples, it was determined that there was less than 0.5 mole percent alumina solubility in zirconia. Optical and X-ray analysis indicated the possibility of solid solution of the compound known as CA_2 since the stoichiometry at 1500 °C was more nearly C_3A_7. Long term changes in calcia solubility in cubic zirconia were studied for up to 2000 hours in samples which had been sintered at 1550 °C. These studies were made at 900 °C and 1300 °C. Solubility changes were measured by quantitative X-ray analysis and by measuring changes in lattice parameter dimensions of cubic zirconia. Evaluation of several samples fired at 1700 °C indicated that melting had occurred and that equilibrium was not attained.

Qualitative Phase Diagram at 1500 °C

Using the phases present as obtained from qualitative X-ray diffraction analysis of series 2 and series 3 samples, Appendix B, estimated Alkemade lines were drawn to divide the three phase regions which were obtained, Figure 10. The crystalline phases found in each sample after

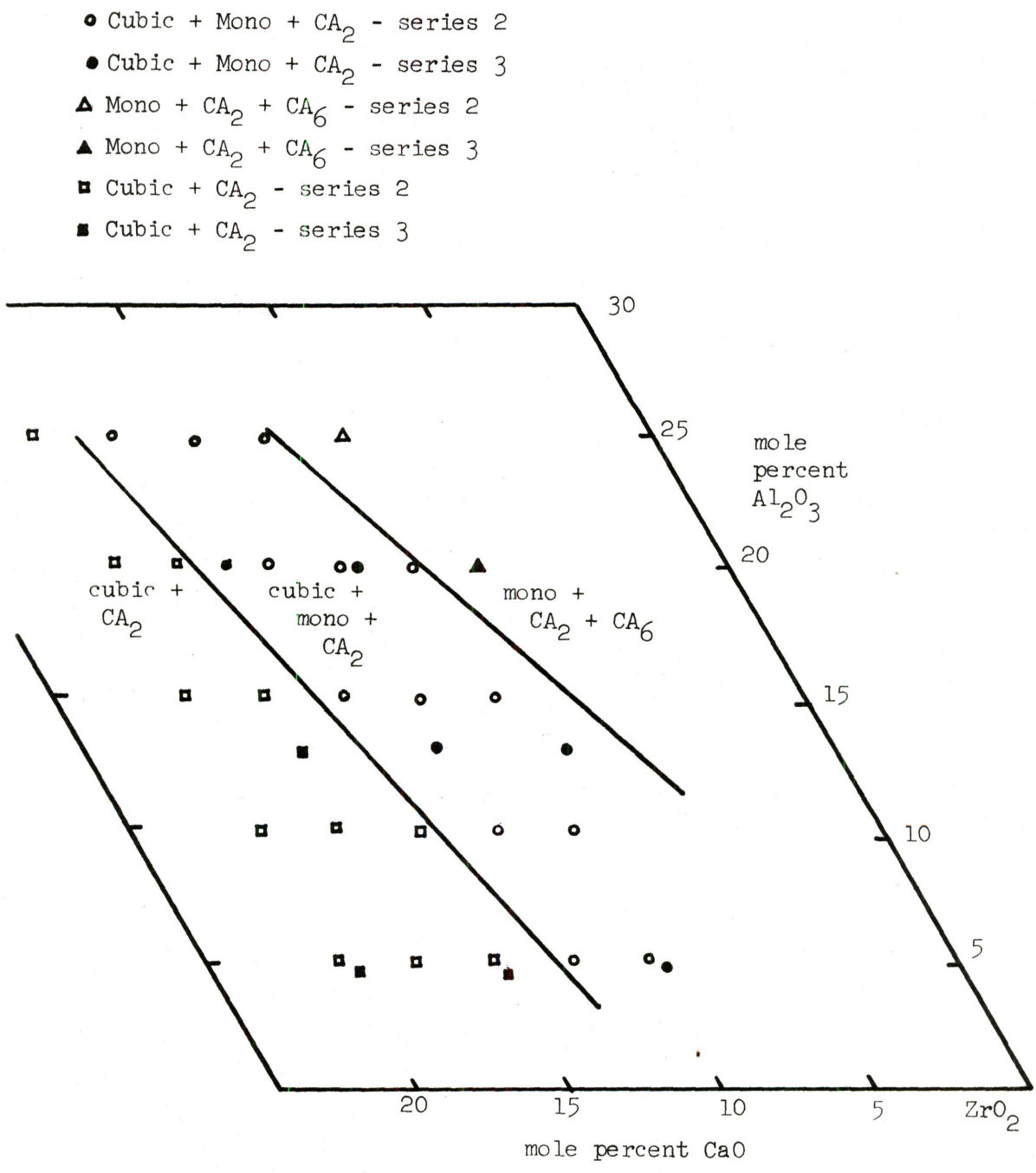


Figure 10. Phase Analysis of Samples Slow-Cooled from 1500 °C

firing for 20 hours and slow cooling were identical to those found in the samples after firing for 40 hours and water quenching. From these qualitative results at 1500 °C, equilibrium appeared to have been obtained, but the question was approached more rigorously in the following section. From phase equilibria theory, a two phase region should divide the CA_2 + CA_6 + monoclinic zirconia area from the CA_2 + cubic zirconia + monoclinic zirconia area. No sample with only CA_2 + monoclinic zirconia was found, but it is certainly reasonable that the region is almost the width of a line and that no composition was chosen for analysis that fell exactly on that line.

Calculation of Alkemade Lines and Verification of Equilibrium at 1500 °C

In order to calculate the exact position of the CA_2 - cubic and CA_2 - monoclinic Alkemade lines, the cubic and monoclinic zirconia peak heights from the X-ray scan for each sample were used to determine quantitatively the weight ratio of cubic zirconia to monoclinic zirconia in each sample that contained both phases. These weight ratio values were converted to a mole basis to be compatible with the remaining quantitative information which was in mole percent. For conversion the composition of cubic zirconia was assumed to be 13 mole percent CaO and 87 mole percent zirconia. No significant variation in the values would have been obtained if a composition for cubic zirconia of 16 mole percent calcia, which is also suggested in the literature, had been used. The assumption was also made that monoclinic zirconia was 100 percent zirconia. This assumption is justified since no more than one mole percent calcia exists in monoclinic zirconia, from published phase diagrams. The cubic zirconia

to monoclinic zirconia Alkemade line must also be assumed to lie at a constant mole percent alumina. With these assumptions made, it may be stated that the ratio of cubic zirconia to cubic plus monoclinic zirconia varies linearly from 0 to 1 on any constant mole percent alumina line across the compatibility triangle. Thus the exact position of the Alkemade lines may be determined from quantitative X-ray data.

To predict the two Alkemade lines intersecting at CA_2 and bounding the cubic + monoclinic + CA_2 phase region, the cubic : (cubic + monoclinic) ratio was plotted versus the mole percent calcia of samples containing a constant mole percent of alumina, Figure 11. These relationships were then extrapolated using a linear regression program to determine the endpoints, which are points on the Alkemade lines. The calcia contents at 0 percent and 100 percent cubic at various alumina contents were used to calculate, again by the linear regression method, the equations of the two Alkemade lines. Appendix C contains the data from measuring cubic to monoclinic ratios and the calculated mole basis.

Initially, equations for the lines for the slow cooled series 2 samples were determined as follows:

$$\% \text{ CaO at } 100 \% \text{ cubic} = 0.29\ (Al_2O_3) + 11.09 \qquad (5)$$

$$\% \text{ CaO at } \quad 0 \% \text{ cubic} = 0.56\ (Al_2O_3) + 2.58. \qquad (6)$$

In order to prove that equilibrium had been reached, the same procedure for calculating the two Alkemade lines was performed for the series 2 samples after they had been refired for a second 20 hours and quenched. The equations determined for these two lines were as follows:

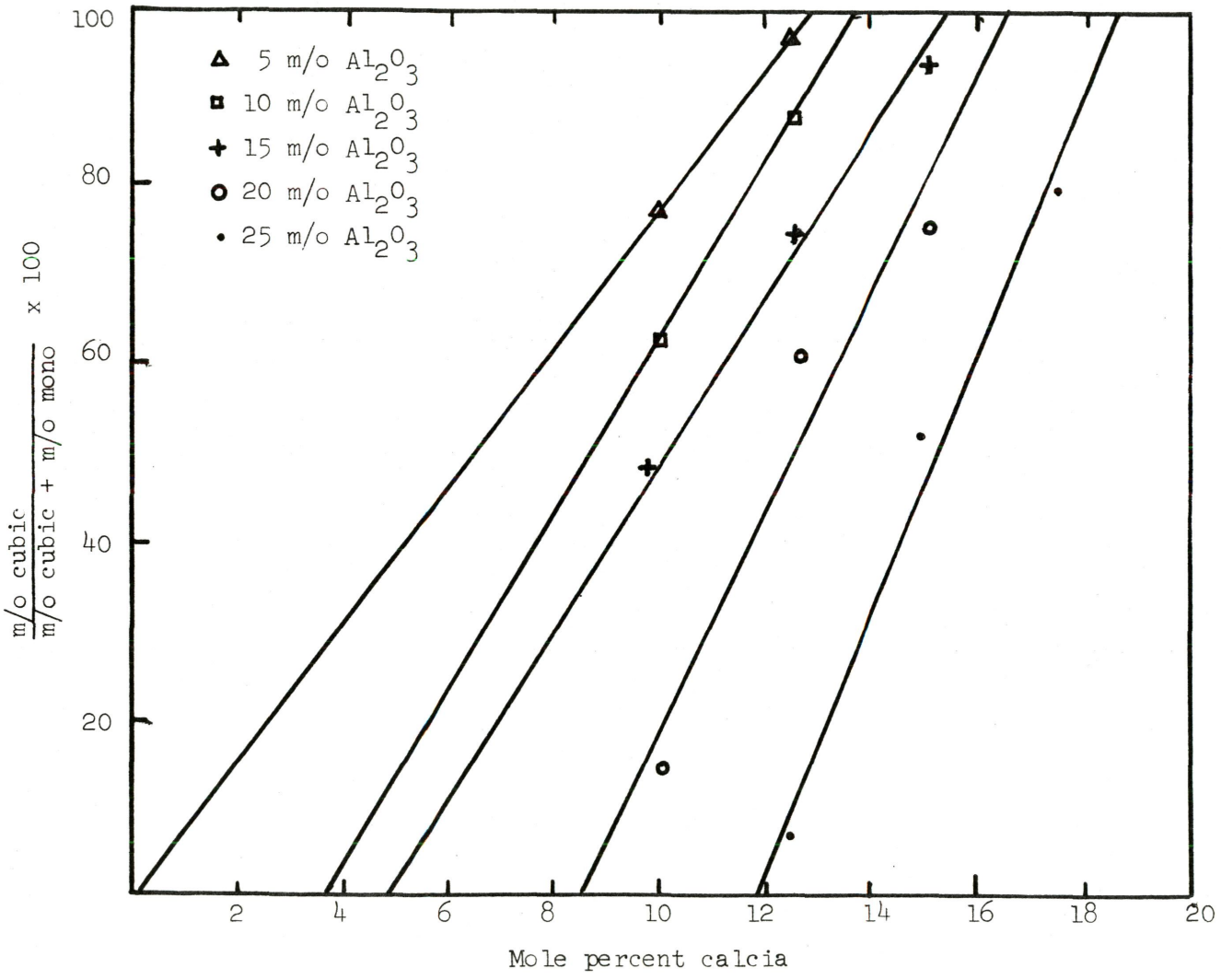


Figure 11. Extrapolation of Calcia Content to 0% and 100 % Cubic Zirconia at Fixed Alumina Contents

$$\% \text{ CaO at } 100 \% \text{ cubic} = 0.26\ (Al_2O_3) + 11.8 \qquad (7)$$

$$\% \text{ CaO at } \quad 0 \% \text{ cubic} = 0.53\ (Al_2O_3) - 2.25\ . \qquad (8)$$

As can be seen in Figure 12, within the limits of experimental error, a close agreement exists between the Alkemade lines determined at 20 and 40 hours. This agreement demonstrates that the slow cooled series 2 samples had reached equilibrium after being fired for 20 hours, since there was no change after a second 20 hour firing and quenching.

Examination of the series 3 quantitative results indicated that there was good agreement with the series 2 results. This observation indicated that the method of preparation did not affect the resulting phases, as should be expected if equilibrium had been reached. Thus alumina may be added to stabilized zirconia with the same results as mixing calcia, alumina, and monoclinic zirconia in one operation.

In order to obtain the most accurate lines, since all three sets of data (series 2 slow cooled, series 2 quenched, and series 3) were in agreement, the cubic to monoclinic ratio for all of the samples was used to calculate the two Alkemade lines, Figure 13. The equation of the CA_2-cubic zirconia line was as follows:

$$\% \text{ CaO at } 100 \% \text{ cubic} = 0.28\ (Al_2O_3) + 11.58, \qquad (9)$$

and the equation of the CA_2 - monoclinic zirconia line was as follows:

$$\% \text{ CaO at } 0 \% \text{ cubic} = 0.48\ (Al_2O_3) - 0.89\ . \qquad (10)$$

Alumina Solubility in Cubic and Monoclinic Zirconia

The solid solution region along the calcia-zirconia binary line

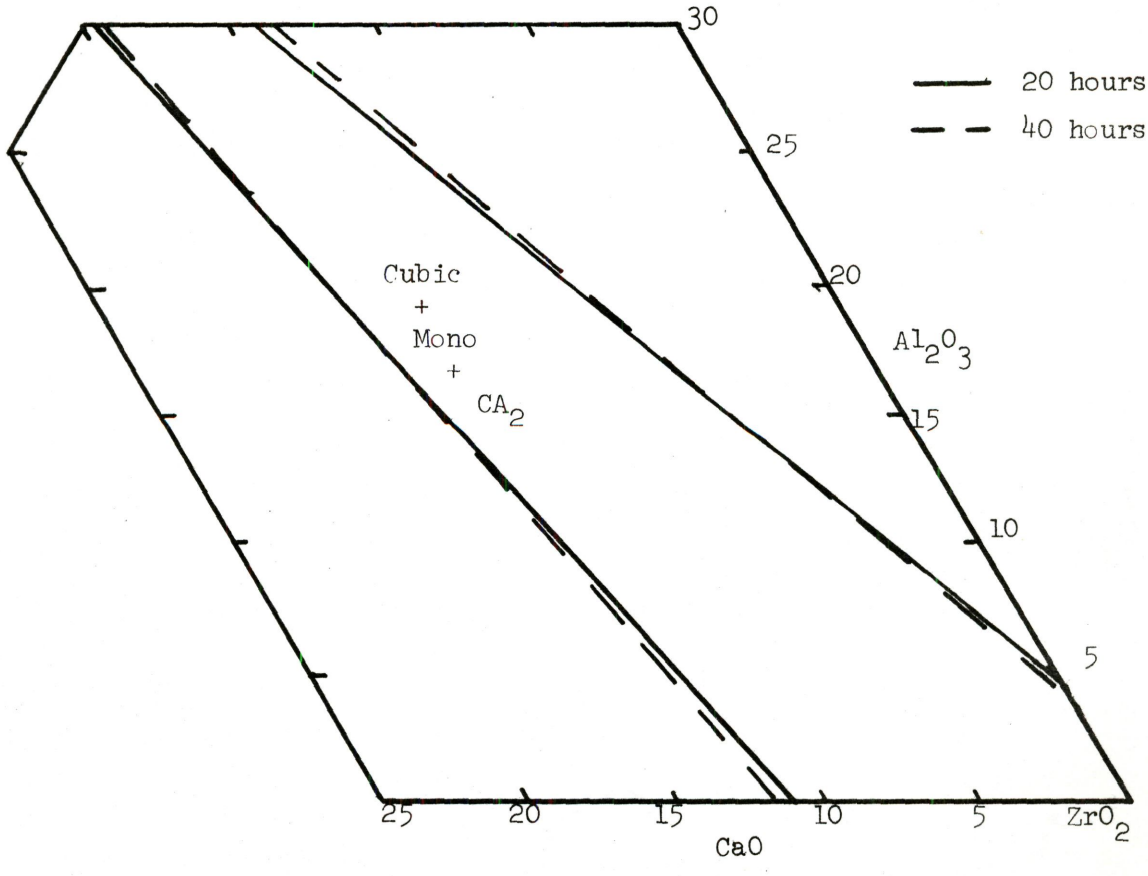


Figure 12. Cubic Zirconia Alkemade Lines at 20 and 40 Hours Firing at 1500 °C, Verifying Equilibrium by Reproducibility of Lines

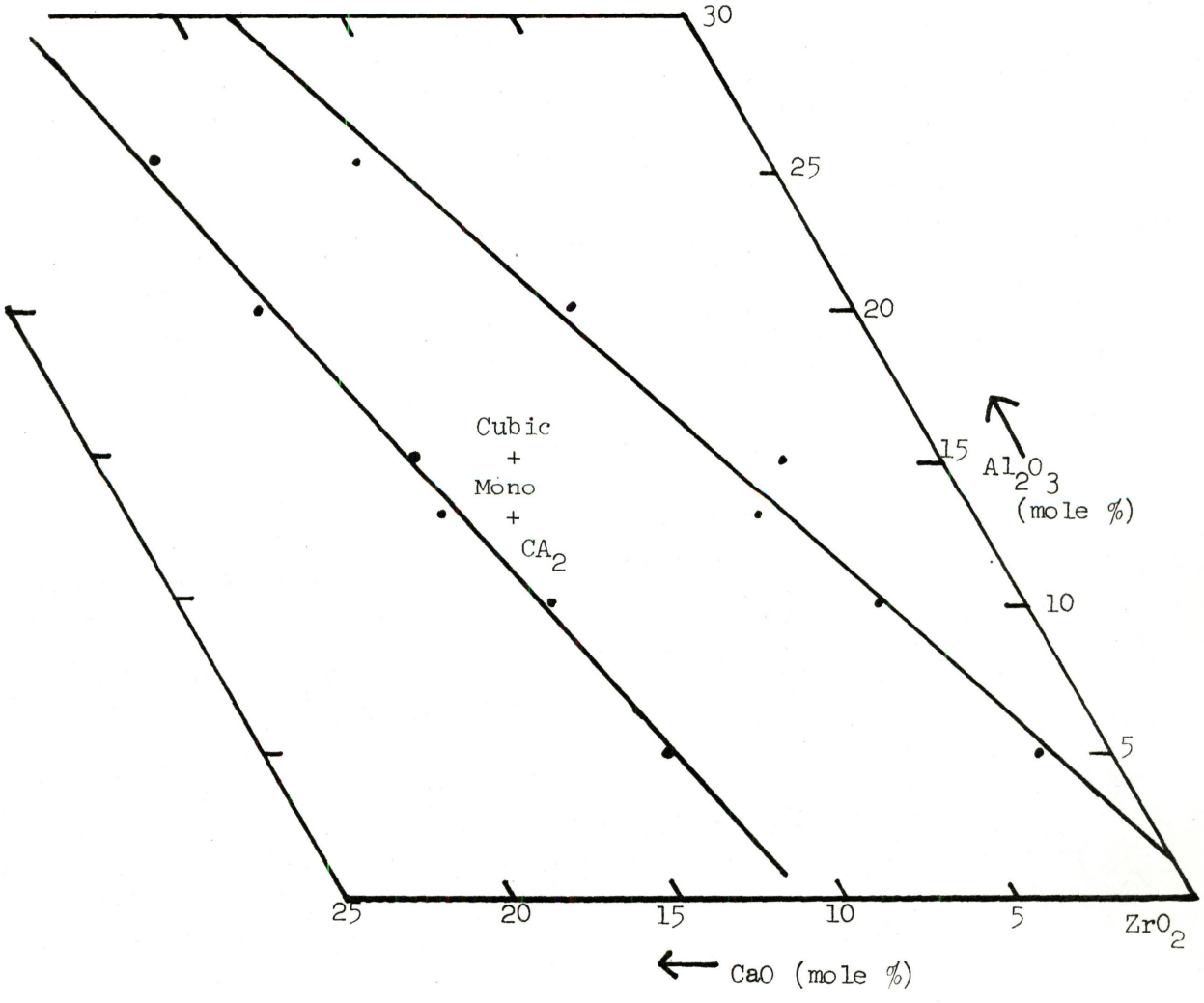
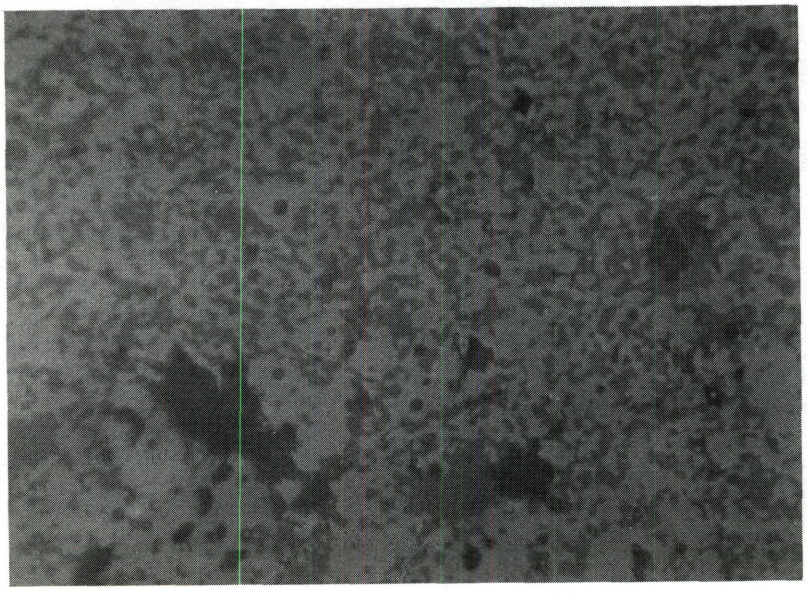


Figure 13. Alkemade Lines Bounding the Cubic + Monoclinic + CA_2 Region at 1500 ^{o}C

for alumina has been estimated from information in the literature and from optically determined CA_2 volume contents. Takagi[6] indicated that at 0.5 weight percent alumina he saw a calcium aluminate phase when samples were fired at 1700 °C. This observation suggests that the region of alumina solubility does not extend as much as 0.55 mole percent above the line. Quantitative X-ray analysis could not be used to determine the amount of CA_2 present in each sample because a sufficiently pure sample of CA_2 was not available.

From the optical data, an estimate was made of the compositions at which the CA_2 phase disappeared and reached 100 %. Samples 2-2, 3-1, 3-5, 2-25, and 3-9 were chosen since they lay on a line drawn from CA_2 to a composition of eight mole percent calcia and 92 mole percent zirconia. The photographs of two samples, 3-1 and 3-9 are shown in Figure 14 as examples of the microstructures which were observed. A method similar to that used for determining the position of the Alkemade lines was used. The volume percents of the CA_2 phase were converted to weight percents, assuming a 2:1 weight ratio of cubic to monoclinic zirconia and densities of 6.15 g/cc for cubic zirconia, 5.83 g/cc for monoclinic zirconia, and 2.89 g/cc for CA_2. Weight percents were converted to mole percents assuming that CA_2 was exactly a 1:2 ratio and that the other end point of the tie line was at eight mole percent calcia and 92 mole percent zirconia. Table 10 shows the data as converted. Mole percent CA_2 was plotted versus mole percent Al_2O_3 and with a linear regression program the best line fit was determined, Figure 15. Extrapolation to 100 % CA_2 gave a stoichiometry for CA_2 of 69.2 mole percent alumina and 30.8 mole percent calcia,

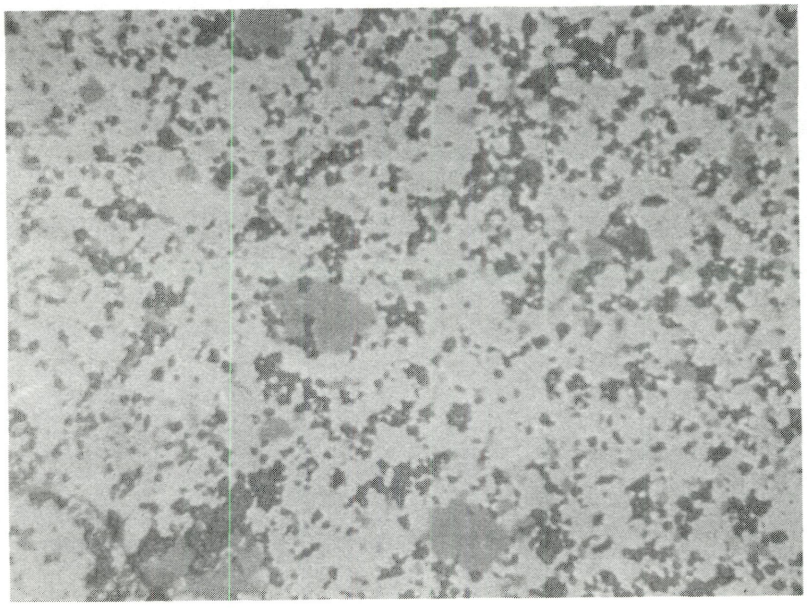


Sample 3-1

ZrO_2 64 m/o

CaO 16 m/o

Al_2O_3 20 m/o



Sample 3-9

ZrO_2 85.7 m/o

CaO 9.5 m/o

Al_2O_3 4.8 m/o

Figure 14. Photomicrographs of Series 3, 1500 ^{o}C, 600x

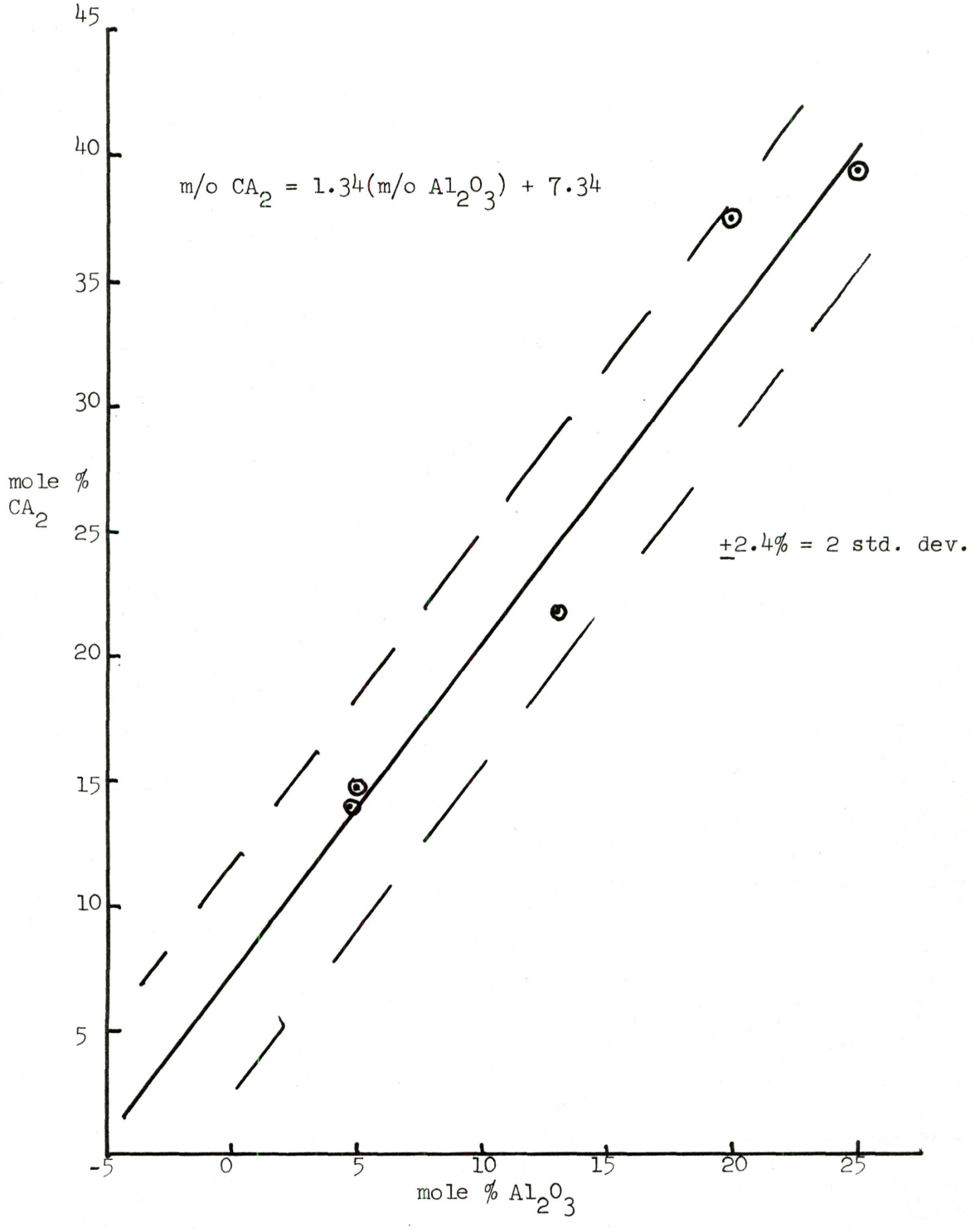


Figure 15. Extrapolation of CA_2 Composition to 0% Alumina to Determine Al_2O_3 Solubility in Zirconia

Table 10. Optical data for CA_2 Stoichiometry Determination

Sample Number	m/o CaO	m/o Al_2O_3	vol % CA_2	wt % CA_2	m/o CA_2
2-2	17.5	25.0	50	32.35	39.4
3-1	16.0	20.0	48	30.63	37.5
3-5	13.0	13.0	30	17.01	21.8
2-25	10.0	5.0	21	11.28	14.7
3-9	9.5	4.8	20	10.68	14.0

which is closer to C_3A_7 than CA_2. Extrapolation to 0 % CA_2 resulted in a negative alumina value, which is obviously erroneous, but does suggest that very little alumina exists in solid solution in either zirconia phase, as noted by Takagi.[6]

CaO-Al_2O_3-ZrO_2 Phase Equilibria at 1500 °C

From the data presented above plus information obtained from the literature, it is possible to construct a phase diagram of the high zirconia region of the calcia-alumina-zirconia ternary system at 1500 °C, Figure 16. The CA_2 - cubic zirconia and CA_2 - monoclinic zirconia Alkemade lines determined above are shown solid because they have been accurately determined. From equation 9, the Alkemade line extrapolation to 0 % alumina, the boundary between the cubic + CA_2 region and the cubic + monoclinic + CA_2 region is placed at 11.6 mole percent CaO, rather than the 13 to 16 mole percent reported by other investigators. The cubic zirconia - monoclinic zirconia Alkemade line is drawn at 0.5 mole percent alumina, as described above.

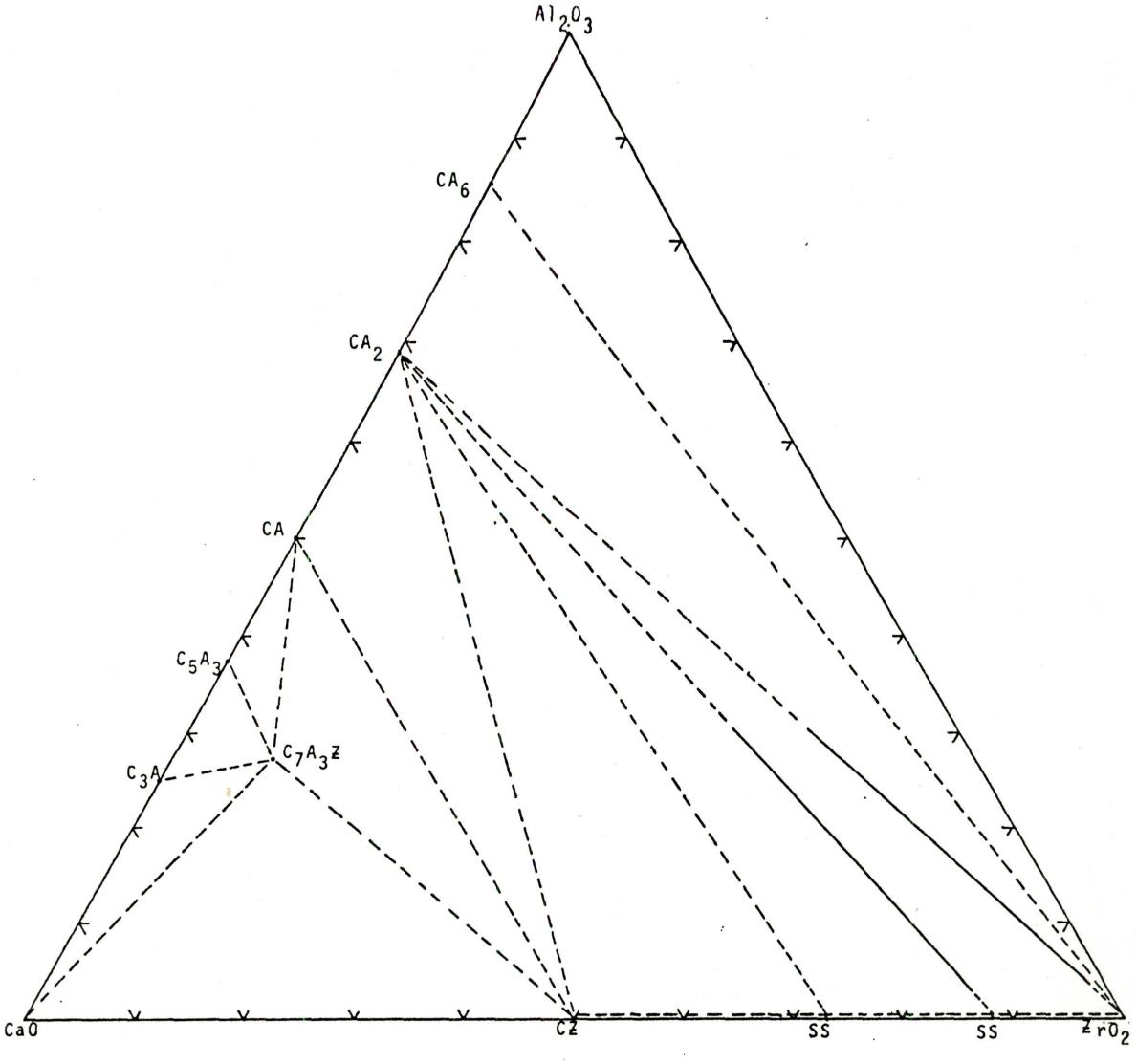


Figure 16. Calcia-Alumina-Zirconia Phase Diagram at 1500 °C

The fact that the Alkemade lines from CA_2 to cubic zirconia and from CA_2 to monoclinic zirconia intersected the Al_2O_3 - CaO binary at 69 mole percent Al_2O_3 and 31 mole percent CaO and also that the CA_2 volumes extrapolated to 100% resulted in the same Al_2O_3 - CaO composition for CA_2 may prove to be significant. Because the extrapolations were made from the high zirconia region to the low zirconia region, experimental error may have produced the indicated deviation from CA_2 stoichiometry. However, if these results were accepted, then CA_2 must exist as a solid solution. From the data obtained, the stoichiometry was closer to C_3A_7, but no where in the literature was any suggestion of this possibility made. Determination of the CA_2 lattice parameters at various temperatures would show if the CA_2 stoichiometry were changing, but because the CA_2 crystal structure is monoclinic, accurate calculation is very difficult. An attempt at determining the lattice parameters of CA_2 was made by assuming that the lattice angles remained unchanged, but the results were extremely scattered, indicating that only a low degree of accuracy was possible. Because of the lack of agreement in the literature about the structure of CA_2, different investigators may have arrived at different solid solution compositions of the same compound, depending on their method of preparation or the raw materials used. A small amount of zirconia may possibly have entered the CA_2 lattice, which would alter the results of quantitative X-ray analysis as calculated from the data. More investigation needs to be done concerning the structure of CA_2 in the presence of zirconia.

The Alkemade line from the high calcia cubic zirconia to CA_2 was

estimated from the calcia-zirconia binary diagram by Duwez[9] as was the line from CZ to CA_2. To confirm qualitatively that the regions were labeled correctly, three samples in the cubic + CZ + CA_2 triangle and one in the CA_2 + CZ + CA triangle, series 4 samples, were fired and analyzed by X-ray. No quantitative or other exhaustive analysis was performed. Phase analysis by X-ray did confirm that the two triangles were drawn properly. The Alkemade line from monoclinic zirconia to CA_6 is also drawn from literature data.[1] Samples 2-5 and 2-10 did confirm the composition of the region to be monoclinic + CA_2 + CA_6. The phase diagram at greater than 50 mole percent calcia is drawn from the investigation of Berezhnoi[1].

Upon original x-ray examination of samples 2-11, 2-12, 2-16, 2-21, and 2-22, an additional phase was found to be present in small amounts. Identification from JCPDS File Cards indicated that the phase was $4CaO \cdot 3Al_2O_3 \cdot SO_3$. The chemical analysis of the TAM zirconia which was used as a raw material showed an SO_2 content of 0.1%, which was apparently enough for this additional phase to appear on the surface of the samples. When the surface of the pellets was gound off with silicon carbide grinding paper, this phase disappeared in the X-ray scans. Since the phase appeared only on the surface and was caused by an impurity, further consideration was omitted and the surface of each sample was ground sufficiently to eliminate what was considered to be a contaminant.

Long Term Phase Equilibria Stability

Changes in the amount of solubility of calcia in cubic zirconia were studied for up to 2000 hours at 900 °C and 1300 °C. Quantitative

X-ray analysis was used to study the destabilization of cubic zirconia. Lattice parameter measurements were made to confirm the indicated amount of destabilization.

Quantitative X-Ray Analysis

Three compositions were chosen in the cubic zirconia + monoclinic zirconia + CA_2 compatibility triangle for determining the stability of the phases over periods of time up to 2000 hours of firing. Two temperatures, 900 °C and 1300 °C, were chosen for experimentation since these seemed to be temperatures at which industry might use these compositions as refractories. The three compositions were chosen at points where the cubic to monoclinic zirconia weight ratio was approximately 3:1 as determined from the results of the 1500 °C analysis. Sample A was 10.0 mole percent alumina and 12.5 mole percent calcia, sample B was 17.5 mole percent alumina and 14.5 mole percent calcia, and sample C was 25 mole percent alumina and 17.5 mole percent calcia.

The three compositions were initially fired at 1550 °C in order to densify the pellets more completely than at 1500 °C. X-ray analysis of the fired pellets showed that even a 50 °C increase in temperature had significantly increased the weight ratio of cubic to monoclinic zirconia compared to the contents at 1500 °C. This change in weight ratio indicated that one of the solid solution endpoints changed considerably. The analysis of sample C showed no monoclinic zirconia at 1550 °C, which meant that the Alkemade line had moved to a CaO content lower than this composition point. In order to calculate the position of the CA_2 - cubic zirconia Alkemade line, it was assumed that the Alkemade line joining

CA_2 and monoclinic zirconia did not move, since Duwez[9] and Hennicke[25] both indicated that there was very limited solid solution in monoclinic zirconia. From the equation for the CA_2 - monoclinic zirconia line at 1500 °C, the CaO content at 10, 17.5, and 25 mole percent alumina (compositions A, B, and C respectively) was determined. Using the calcia contents at 0% cubic zirconia and the ratio of cubic to cubic plus monoclinic zirconia at the three compositions, the 100 % cubic line was calculated as described for 1500 °C, Figure 17. Since there was only one data point at each alumina composition, the location of the line could not be determined as accurately as the 1500 °C line was established. The implication from the position of the 1550 °C line is that the composition of CA_2 was varying more than the composition of the cubic zirconia. Because only three data points were available, this conclusion is open to question. It must also be stated that if the CA_2 composition were changing with temperature increase, then the CA_2 - monoclinic zirconia Alkemade line would also be changing; thus the 1500 °C line equation would not be valid for determining the second data point at each alumina composition. However, from lattice parameter measurements for cubic zirconia, to be presented below, it will be shown that CaO solid solution changes in zirconia resulted in the Alkemade line movement.

Quantitative X-ray results of the surface scans of the long term fired samples after firing at 900 °C and 1300 °C were inconsistent, particularly for the samples being held at 900 °C. The pellet surfaces were ground to remove approximately 1 mm and consistency was obtained. Further grinding showed no changes in the weight ratios of cubic to monoclinic

At 1550 °C for 100% cubic zirconia: %CaO = 0.26 (Al_2O_3) + 11.14

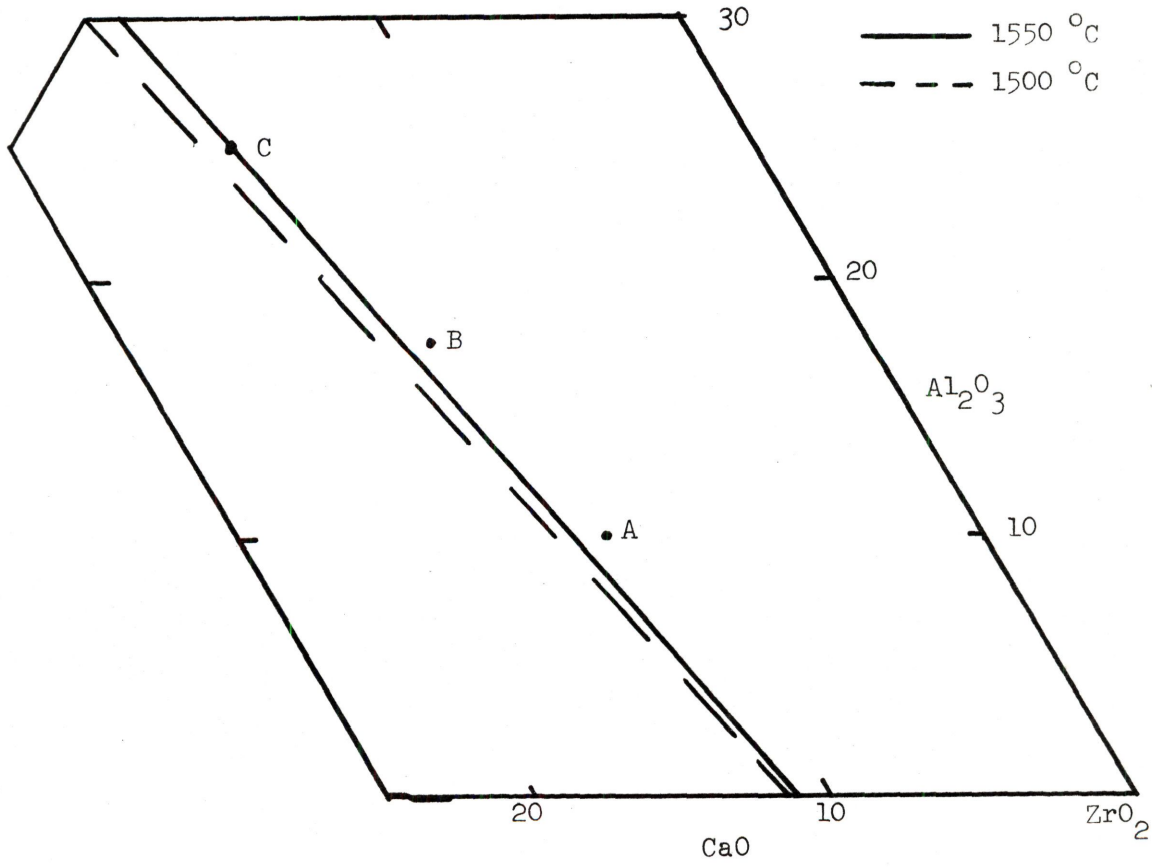


Figure 17. Alkemade Line at 1550 °C from CA_2 to Cubic Zirconia

zirconia. The quantitative X-ray results for the long term fired samples are presented in Appendix D. Changes in the ratio of cubic zirconia to cubic plus monoclinic zirconia, Figures 18 and 19, give a clear indication of phase changes with respect to time.

At 1300 °C little problem existed with surface inconsistencies, as results obtained from a lightly ground surface agreed well with a 1 mm surface removal. A considerable decrease in the amount of cubic zirconia with firing time can be seen. By 1000 hours equilibrium had been reached, as indicated by a constant cubic to cubic plus monoclinic ratio from 1000 to 2000 hours. It may be noted that sample C must be very close to the boundary because its composition changed radically in the first 400 hours. Samples A and B changed in the same direction but to a lesser extent.

The Alkemade line from CA_2 to cubic zirconia at 1300 °C was determined by the same method as was used at 1550 °C, and thus not too great an accuracy could be implied. The calculated position, Figure 20, indicates that approximately a three mole percent increase occurred in the calcia content of cubic zirconia from 1500 °C to 1300 °C. The increase was slightly more than expected from results reported by Duwez[9], but the data is limited, and therefore not conclusive.

At 900 °C the destabilization Process took place very slowly. Sample C showed this process most clearly, in that the X-ray data indicated no monoclinic zirconia for 1000 hours and only a slow increase from 1000 to 2000 hours. Changes in samples A and B are almost imperceptible. After about 1400 hours sample A appeared to begin to destabilize. In sample B there was no perceptible change in the weight ratio of cubic to

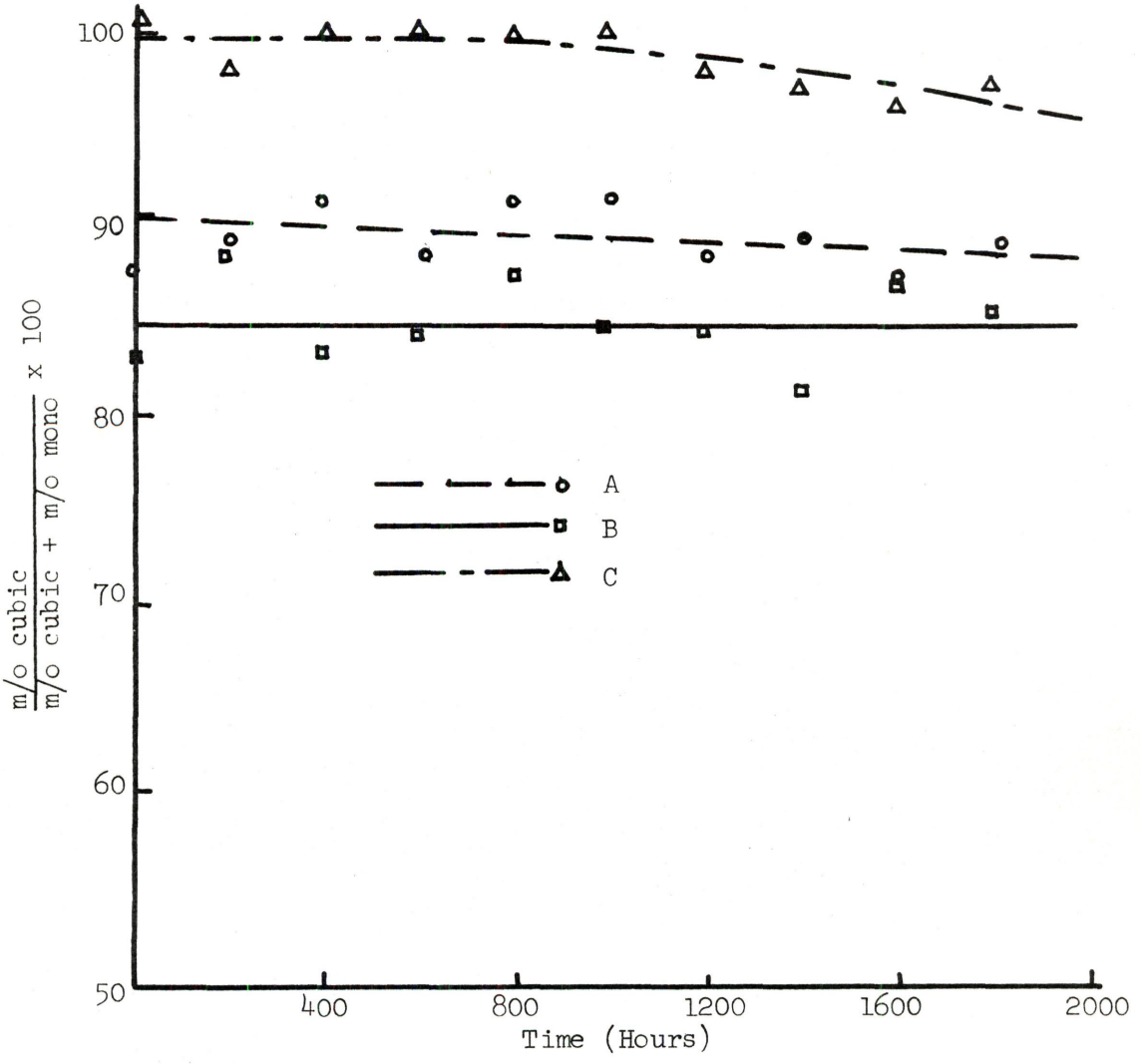


Figure 18. Change in Amount of Cubic Zirconia with Time at 900 °C

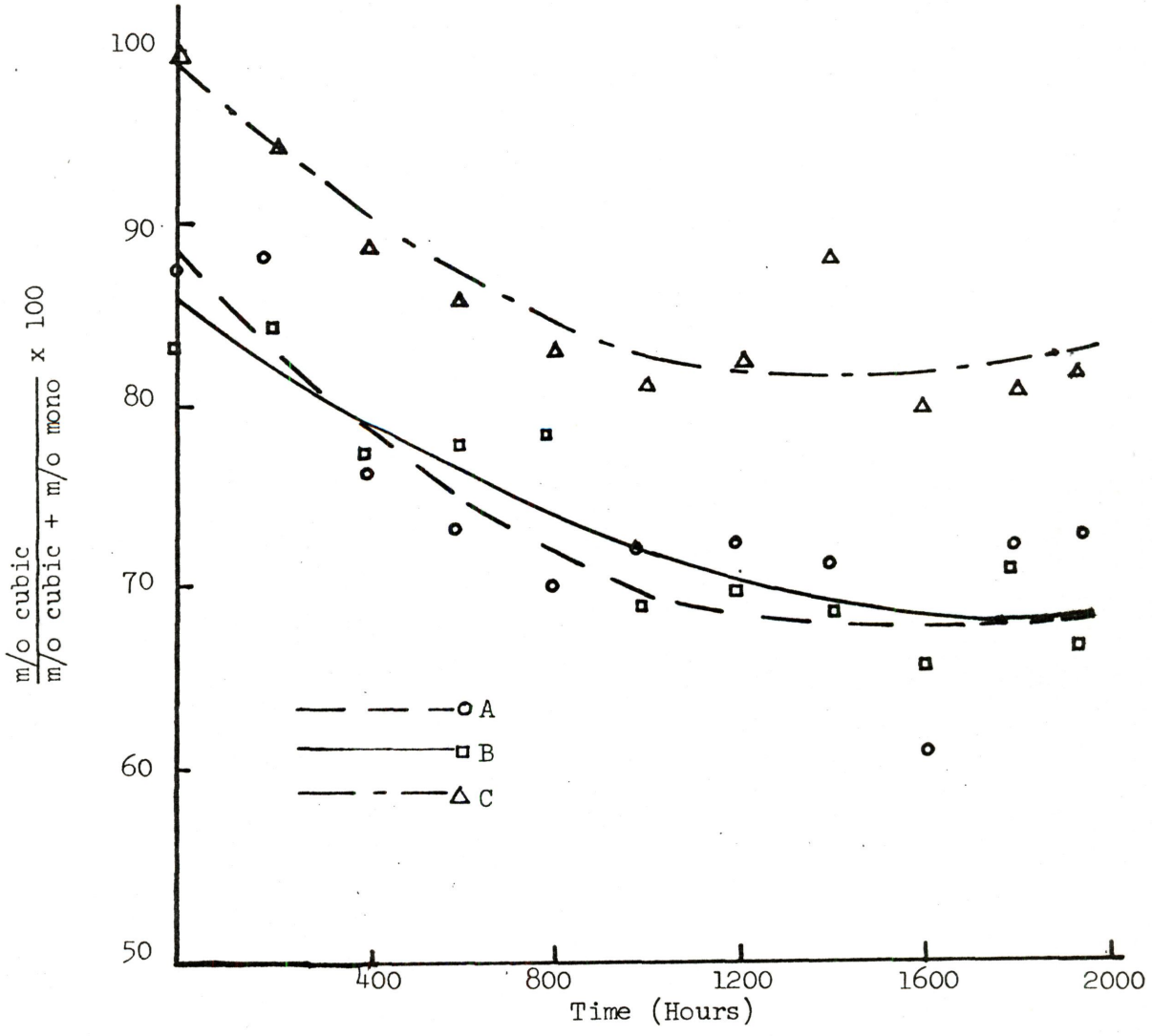


Figure 19. Change in Amount of Cubic Zirconia with Time at 1300 °C

At 1300 °C for 100% cubic zirconia: %CaO = 0.17 (Al_2O_3) + 14.6

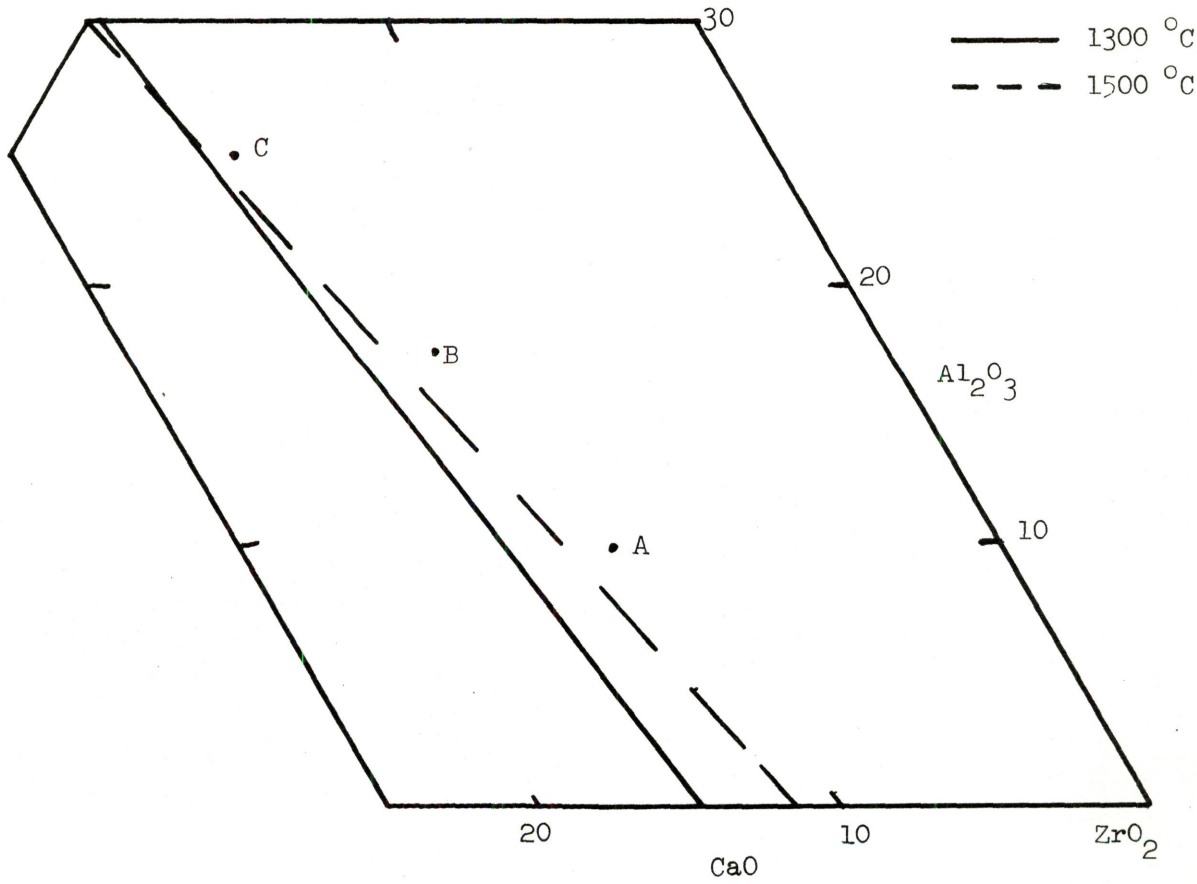


Figure 20. Alkemade Line at 1300 °C from CA_2 to Cubic Zirconia

monoclinic zirconia. Thus with the cubic to monoclinic ratios showing little change from 1550 °C, the samples are not near equilibrium, even after 2000 hours. From thermal expansion measurements made on these samples in related work[28], the monoclinic zirconia content was found to be increasing even at 200 and 400 hours for each of the samples at 900 °C, but the change was small, indicating that only a slight amount of destabilization was occurring in samples fired to 1550 °C. Because equilibrium was not attained at 900 °C, no estimation of the tie line at this temperature could be made.

At 900 °C the above data agrees well with the results obtained by Duwez[9] for long term stability of a pure calcia stabilized zirconia. At 1300 °C, though, he found much better stability of calcia stabilized zirconia than was indicated for calcia stabilized zirconia with alumina additions. For samples A and B the actual amount of destabilization at 1300 °C may not be enough to cause a practical problem. For instance, sample A changed from a composition that was 11.0 weight percent monoclinic zirconia at 1550 °C to one that was 25.0 weight percent monoclinic zirconia at 1300 °C. Measurements of the coefficients of linear thermal expansion might show a small enough change that the thermal shock characteristics would not be adversely affected. Even the change in sample C from a cubic zirconia composition to one that was 10.8 weight percent monoclinic might not be enough of a change to cause a problem in actual use. This particular area is one in which more work must be done.

Lattice Parameter Determinations for Cubic Zirconia

In order to study changes in the structure of the zirconia cubic solid solution, the lattice parameter was determined for samples at 0,

200, 1000, and 2000 hours at both 900 °C and 1300 °C and for the 1300 °C samples also at 400 hours. A lattice parameter value of 5.126 for the samples as fired at 1550 °C agrees better with the data published by Garvie[10] than with that of Duwez[9]. Figure 21 shows the averaged lattice parameters of samples A, B, and C versus time and includes the variations which were observed. The 1300 °C data is as expected. Both Duwez and Garvie indicated that a variation in a of 0.003 A represents approximately a change in composition of two mole percent calcia. Thus the change in lattice parameter from 1550 °C to 1300 °C agrees well with the calculated measurement of the Alkemade line. The phase diagram of the calcia-zirconia binary by Duwez also confirms the results. The samples fired at 1550 °C have about two mole percent less calcia than those that have reached equilibrium at 1300 °C.

The lattice parameter results for the 900 °C samples cannot be understood strictly from a crystal structure point of view. With the cubic zirconia being the highest thermal expansion phase present, cooling the samples from 1550 °C apparently resulted in enough tension in the lattice to expand it slightly. On reheating, annealing at 900 °C, and cooling, the lattice expansion due to tension is less, because the temperature change is smaller. Thus annealing at 900 °C with no composition change could result in a decrease of the cubic zirconia lattice parameter. From quantitative X-ray measurements equilibrium was shown not to have been attained at 900 °C even after firing for 2000 hours. If equilibrium at 900 °C were obtained, a larger lattice would have been expected than that found at 1300 °C, due to increasing calcia content. The tension in the lattice is apparently masking the increase in size, and since the

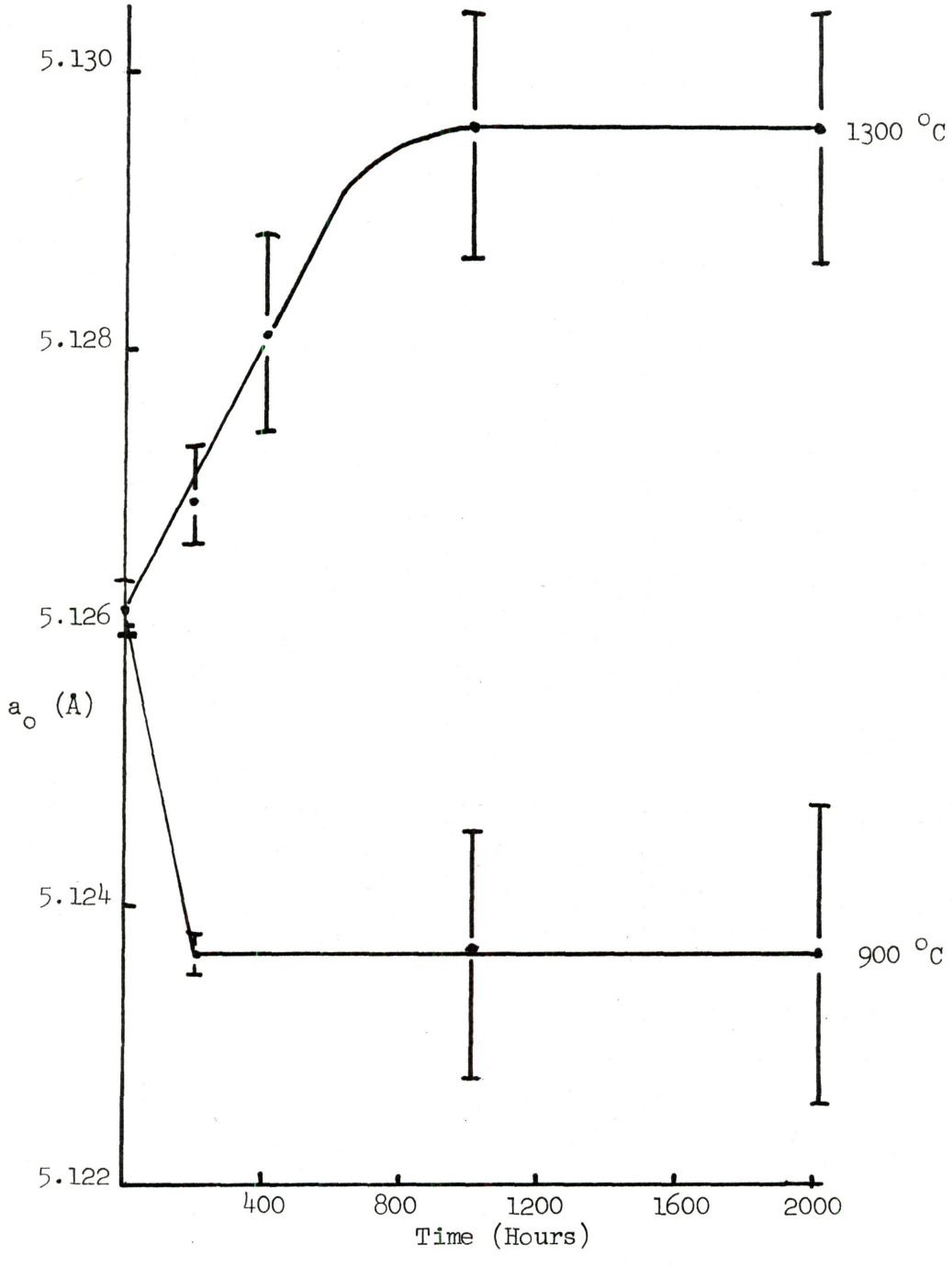


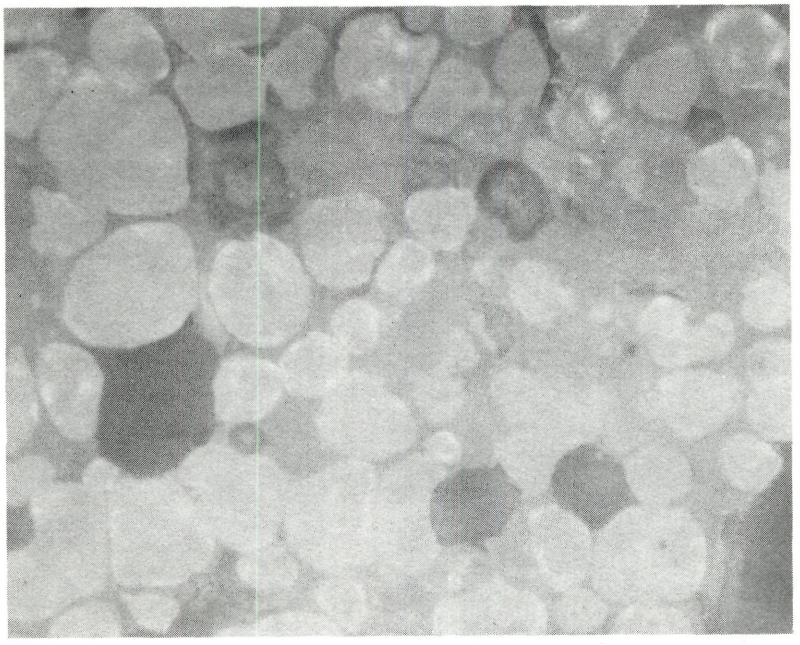
Figure 21. Lattice Parameter Changes with Time

samples were not even near equilibrium, the lattice might not in reality be as large as the 1300 °C lattice at 2000 hours. An effect that cannot be evaluated is the presence of alumina ions, which are half the size of calcia ions. If there were indeed an amount of alumina in the cubic zirconia lattice, then as the amount varied with temperature changes, the alumina could cause the lattice to become smaller, reversing the effect of the addition of calcia. Evaluation of this effect was not possible from the data and equipment available.

Analysis of Series 1 Fired at 1700 °C

When the nine samples 1-1 through 1-9 were removed from the furnace, it was observed that 1-1, 1-2, and 1-4 had definitely undergone partial melting because the edges of the pellets were rounded and slumped. Photographs of samples 1-1 and 1-9 are included, Figure 22, showing large uniformly rounded grains surrounded by the secondary gray phase, which is a clear indication that melting occurred. Table 11 shows the results of the qualitative X-ray analysis and the optical analysis. It is clear from the phase analysis that the samples were not at equilibrium. The phases present do not correspond to the equilibrium phases at 1500 °C and sample 1-1 has four phases present, an impossibility in equilibrium unless the composition was exactly at the eutectic point. Thus no phase diagram information may be taken from these results.

The presence of CA_6 is important. First of all, it corroborates the work of Takagi[6], who also found melting of the samples at 1700 °C, with the formation of CA_6. From the literature it has not been clear if CA_2 melted congruently or incongruently. The presence of CA_6 in several

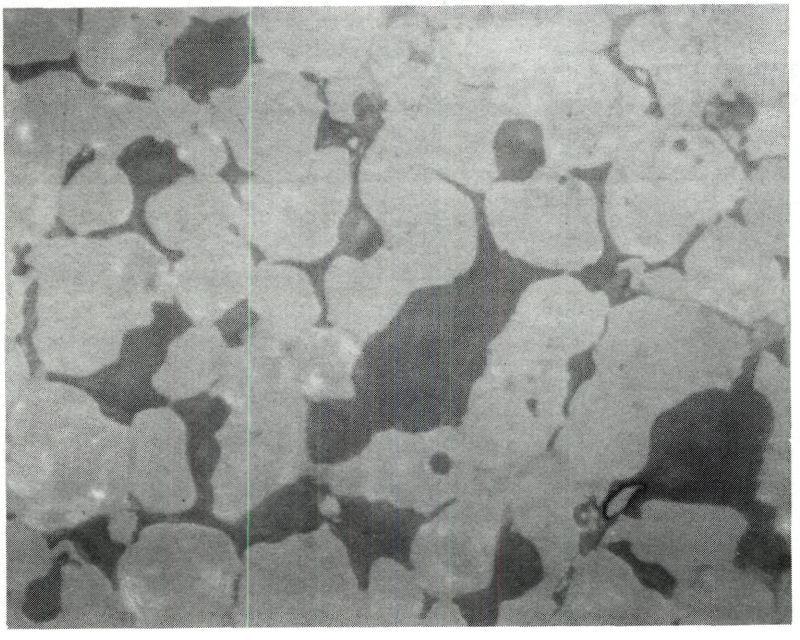


Sample 1-1

ZrO_2 64 m/o

CaO 16 m/o

Al_2O_3 20 m/o



Sample 1-9

ZrO_2 85.7 m/o

CaO 9.5 m/o

Al_2O_3 4.8 m/o

Figure 22. Photomicrographs of Series 1, 1700 °C, 600x

Table 11. Phase Composition and Optically Determined Phase Volume of Series 1, 1700 °C

Sample Number	Crystalline Phases	Percent Porosity	Optical % White	Optical % Gray
1-1	Cubic, CA_6, CA_2, Mono	13	61	39
1-2	Cubic, Mono, CA_2	25	79	21
1-3	Cubic, Mono, CA_6	13	62	38
1-4	Cubic, CA_2, Mono	21	76	24
1-5	Cubic, CA_2	7	69	31
1-6	Cubic, Mono, CA_6	11	78	22
1-7	Cubic, CA_2, CZ	10	84	16
1-8	Cubic, Mono	10	89	11
1-9	Cubic, Mono, CA_6	16	94	6

of the samples, where from previous phase diagram results CA_2 should have been the only calcium aluminate phase, indicates that CA_2 melts incongruently forming CA_6 and a liquid. Thus if the samples did not attain equilibrium on cooling (which was at the relatively fast cool down rate of the gas-fired furnace), it would be reasonable for CA_6 to be present. Much more work must be done to clarify the understanding about CA_2.

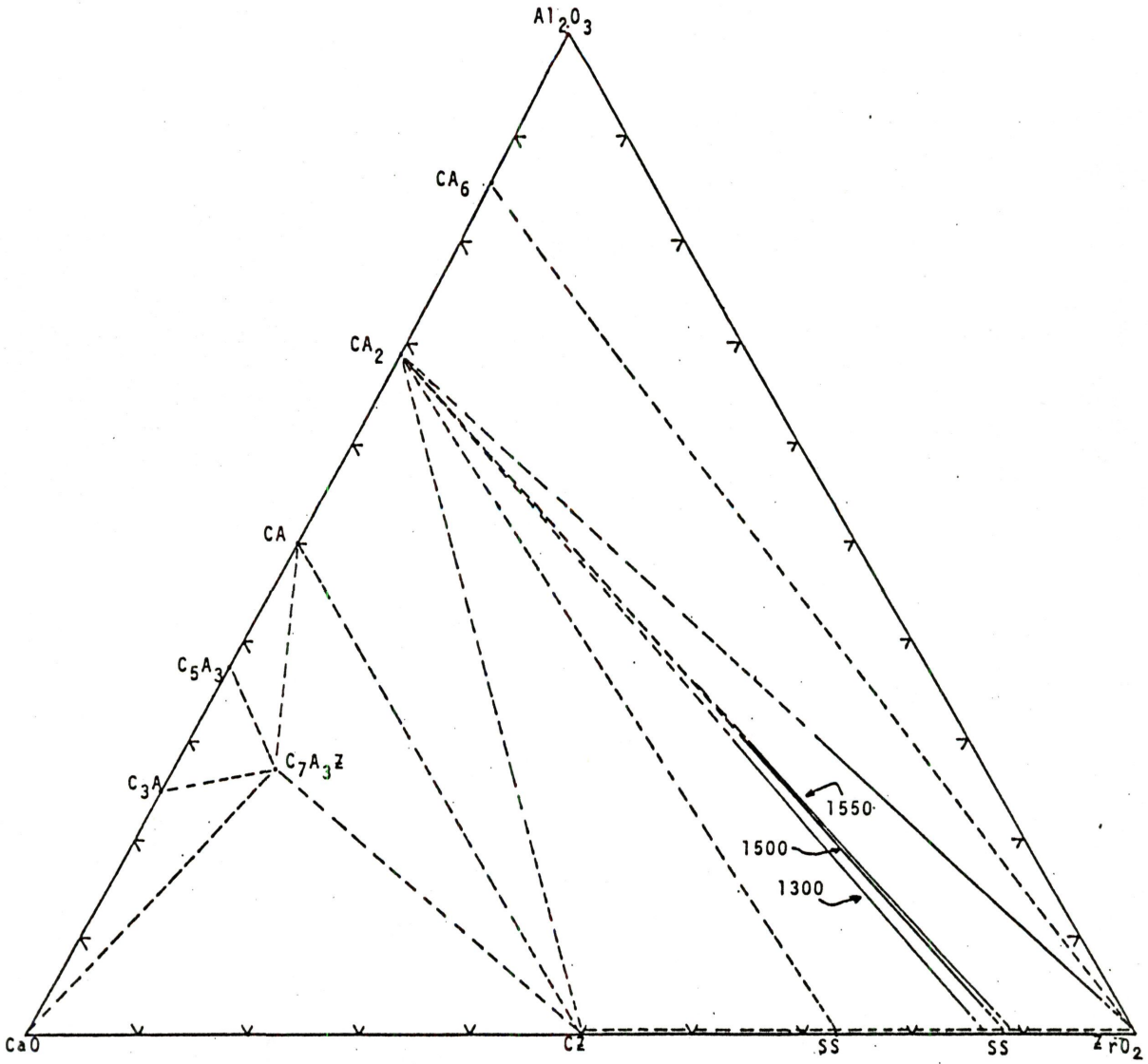
The X-ray phase analysis from sample 1-8 would suggest considerable solid solution of alumina in zirconia. However, the optical information showed that there was still a considerable amount of calcium aluminate in this sample, but that it was below the detection limits of the X-ray diffractometer.

Because equilibrium was not attained because of partial melting of the samples, it was not possible to make any determination about solid solution phenomena for either cubic zirconia or CA_2 at 1700 ^{o}C. The incongruent melting of CA_2 was, however, more definitely established.

CHAPTER V

CONCLUSIONS

1. The phase diagram for the high zirconia region of the calcia-alumina-zirconia system was determined at 1500 °C and combined with available information to prepare a complete phase diagram of the calcia-alumina-zirconia system as shown:



2. The equation of the CA_2 - monoclinic zirconia Alkemade line is

$\%CaO = 0.48\ (Al_2O_3) - 0.89$.

The equation of the CA_2 - cubic zirconia Alkemade line is

$\%CaO = 0.28\ (Al_2O_3) + 11.68$.

3. Solution of Al_2O_3 in cubic and monoclinic zirconia is extremely limited and probably less than one mole percent.

4. The lower limit of calcia solid solution in cubic zirconia varies from 14.6 mole percent at 1300 °C to 11.1 mole percent at 1550 °C.

5. After firing to 1550 °C, the composition of the solid solution cubic zirconia in the CA_2 - cubic ZrO_2 - monoclinic ZrO_2 compatibility triangle required 800 to 1000 hours to reach equilibrium at 1300 °C and changed so slowly at 900 °C that after 2000 hours, equilibrium was not obtained.

6. Calcium di-aluminate, CA_2, melts incongruently to CA_6 plus a liquid.

CHAPTER VI

RECOMMENDATIONS

The behavior of CA_2 should be studied to determine if it really exists as a solid solution and if it changes composition with temperature changes. It should be studied with a small zirconia content in an attempt to ascertain the phase relations of the three component system. A liquidus diagram of the ternary system should also be prepared as a continuation of the phase diagram study. Physical property studies of the samples which were prepared for long term firing would be useful in determining if such compositions might have practical industrial application. In a general sense different areas of the ternary should be studied. The existence of the ternary compound C_7A_3Z claimed by Berezhnoi should be confirmed.

APPENDIX A

SYSTEMATIC POINT COUNTING TECHNIQUE

The systematic point counting technique was used for determining the volume fraction of calcium aluminates, porosity, and zirconia phases from optical micrographs of polished sections of the samples. Accuracy is directly related to the number of points used in the count and the method depends on the fact that the following relationship is true:[29]

$$P_p = V_v \tag{11}$$

where P_p is the fraction of points falling on a phase of interest, and V_v is the volume fraction of the phase of interest. Standard deviation is given by the following formula:

$$\sigma V_v = \frac{V_v}{(N)^{\frac{1}{2}}} \tag{12}$$

where N is the number of points falling on the phase. For a confidence factor of 95%, two standard deviations from the average value are allowed. Table 12 shows the accuracy that can be expected statistically when a total of three hundred points are counted.

Table 12. Accuracy of Systematic Point Counting Technique

V_v	0.01	0.05	0.1	0.2	0.4	0.6	0.8
σV_v	0.006	0.013	0.018	0.026	0.037	0.045	0.052
$\pm$ % accuracy	120	52	36	26	18.5	15	13

Percent accuracy in Table 12 is written in terms of the volume fraction. Accuracy increases as the inverse square of the number of points counted so that, for instance, quadrupling the number of points would only halve the uncertainty. Thus 300 points were determined to be sufficient as a good balance between the time required and the accuracy obtained. A square grid of 25 points spaced on 0.25" centers was dropped randomly without bias on each photograph 12 times as a tally of the points in each phase was made. Randomness was required for accuracy and it was necessary that a representative sector of the sample be photographed, rather than an area with some outstanding feature. The actual numbers determined for volume fractions of the three phases in each pellet were reasonably accurate, within $\pm$ 30% for most cases.

APPENDIX B

PHASE ANALYSIS OF COMPOSITIONS FIRED AT 1500 °C

The phases present were determined qualitatively by X-ray diffraction. Qualitative analysis of series 2 was performed on samples fired for 20 and 40 hours. The results were the same, as listed in the table.

Several of the samples were polished after being fired to 1500 °C and slow cooled. A small amount of porosity, which appeared as very dark areas, was observed. The major phase was white in color and was apparently, as confirmed by quantitative information, the sum of the two zirconia phases. The gray phase was the sum of the calcium aluminate phases, CA_2 and CA_6. The total white and gray phases were expressed in terms of 100%, mathematically eliminating the amount of porosity.

Table 13. Phase Analysis of Series 2

Sample Number	Porosity vol %	White vol %	Gray vol %	Phases Present
2-1	6	49	51	Cubic, CA_2
2-2				Cubic, Mono, CA_2
2-3	8	52	48	Cubic, Mono, CA_2
2-4				Mono, Cubic, CA_2
2-5	13	49	51	Mono, CA_2, CA_6
2-6				Cubic, CA_2
2-7				Cubic, CA_2
2-8				Cubic, Mono, CA_2
2-9	11	54	46	Cubic, Mono, CA_2
2-10				Mono, Cubic, CA_2
2-11	4	65	35	Cubic, CA_2
2-12				Cubic, CA_2
2-13				Cubic, Mono, CA_2
2-14				Cubic, Mono, CA_2
2-15				Cubic, Mono, CA_2
2-16				Cubic, CA_2
2-17				Cubic, CA_2
2-18				Cubic, CA_2
2-19				Cubic, Mono, CA_2
2-20				Cubic, Mono, CA_2
2-21	10	79	21	Cubic, CA_2
2-22				Cubic, CA_2
2-23				Cubic, CA_2
2-24				Cubic, Mono, CA_2
2-25	20	79	21	Cubic, Mono, CA_2

Table 14. Phase Analysis of Series 3

Sample Number	Porosity vol %	White vol %	Gray vol %	Phases Present
3-1	7	52	48	Cubic, CA_2, Mono
3-2	6	56	44	Cubic, CA_2, Mono
3-3	38	65	35	Mono, CA_2, CA_6
3-4	7	67	33	Cubic, CA_2
3-5	24	70	30	Cubic, Mono, CA_2
3-6	24	71	29	Cubic, Mono, CA_2
3-7	9	81	19	Cubic, CA_2
3-8	33	87	13	Cubic, CA_2
3-9	26	80	20	Cubic, Mono, CA_2
3-10				Cubic
3-11				Cubic
3-12				Cubic, Mono

APPENDIX C

DATA FOR CALCULATING CA_2 - CUBIC ZrO_2 AND CA_2 - MONOCLINIC ZrO_2 ALKEMADE LINES

In Tables 15 - 18 are presented the data necessary to calculate the CA_2 - Cubic ZrO_2 and CA_2 - Monoclinic ZrO_2 Alkemade lines. Columns two and three list the Al_2O_3 and CaO composition of each sample on a mole percent basis. The monoclinic to cubic zirconia weight ratio as measured by quantitative X-ray diffraction is in column four. The weight ratio of column four was converted to a mole percent ratio of cubic to cubic plus monoclinic zirconia and is shown in column five. As discussed earlier, at a constant Al_2O_3 mole content, the mole percent ratio of cubic zirconia varies linearly with mole percent CaO from 0 at the CA_2 - Monoclinic zirconia Alkemade line to 100 at the CA_2 - cubic zirconia Alkemade line. Therefore the least squares line fit of mole percent CaO (x) versus mole percent ratio of cubic to cubic plus monoclinic zirconia (y) at constant Al_2O_3 content could be calculated (column six). At each Al_2O_3 content the least squares line was extrapolated to give the mole percent CaO at 100% cubic (column seven) and at 0% cubic (column eight), which are the CaO compositions at that Al_2O_3 composition for the CA_2 - cubic zirconia Alkemade line and the CA_2 - monoclinic zirconia Alkemade line respectively. Linear regression analysis of mole percent CaO versus mole percent Al_2O_3 for the respective lines was used to determine the best fit equations for those two lines, which are presented in Chapter IV.

Table 15. Quantitative X-Ray Data for Series 2 and 3, Slow-Cooled

Sample Number	m/o Al_2O_3	m/o CaO (x)	wt. mono / wt. cubic	m/o cubic (y)	Equation of line	m/o CaO 100 % cubic	m/o CaO 0 % cubic
2-2	25	17.5	0.267	80.1	y= 14.43x - 169.57	18.68	11.75
2-3	25	15	0.962	52.8			
2-4	25	12.5	12.5	7.93			
2-8	20	15	0.345	75.7	y= 10.83x - 90.82	17.62	8.39
2-9	20	12.5	0.684	61.1			
2-10	20	10	6.25	14.7			
3-1	20	16	0.340	76.0			
3-2	20	12	2.78	27.9			
2-13	15	15	0.0558	95.1	y= 9.34x - 43.95	15.41	4.71
2-14	15	12.5	0.361	74.9			
2-15	15	10	1.149	48.4			
3-5	13	13	0.469	69.6	y=10.23x - 63.42	15.97	6.20
3-6	13	8.7	3.125	25.6			
2-19	10	12.5	0.138	88.6	y=10.2x - 38.9	13.62	3.81
2-20	10	10	0.629	63.1			
2-24	5	12.5	0.034	96.9	y= 9.96x - 26.82	12.73	2.69
2-25	5	10	0.316	77.3			
3-9	5	9.5	0.606	64.0			

Table 16. Quantitative X-Ray Data for Series 2, Quenched

Sample Number	m/o Al_2O_3	m/o CaO (x)	wt. mono / wt. cubic	m/o cubic (y)	Equation of line	m/o CaO 100 % cubic	m/o CaO 0 % cubic
2-2	25	17.5	0.0236	97.9	y= 18.81x - 233.77	17.74	12.43
2-3	25	15	1.39	43.6			
2-4	25	12.5	27.03	3.83			
2-8	20	15	0.392	73.3	y= 8.8x - 58.7	18.03	6.67
2-9	20	12.5	1.02	51.3			
2-13	15	15	0.0554	95.1	y= 8.7x - 37.62	15.82	4.32
2-14	15	12.5	0.538	66.7			
2-15	15	10	1.01	51.6			
2-19	10	12.5	0.183	85.5	y= 10.52x - 46.0	13.88	4.37
2-20	10	10	0.741	59.3			
2-24	5	12.5	0.0658	94.2	y= 7.8x - 3.3	13.24	0.42
2-25	5	10	0.365	74.7			

Table 17. Quantitative X-Ray Data for Long-Term Samples at 1550 °C

Sample	m/o Al_2O_3	m/o CaO (x)	wt. mono / wt. cubic	m/o cubic (y)	Equation of line	m/o CaO 100 % cubic	m/o CaO 0 % cubic
A*	10	3.91	infinite	0	y= 10.28x - 40.19	13.64	3.91
A	10	12.5	0.143	88.3			
B*	17.5	7.51	infinite	0	y= 12.06x - 90.57	15.80	7.51
B	17.5	14.5	14.5	0.2			
C*	25	11.11	infinite	0	y= 15.6x - 173.3	17.5	11.11
C	25	17.5	0	100			

Table 18. Quantitative X-Ray Data for Long-Term Samples at 1300 °C

Sample	m/o Al_2O_3	m/o CaO (x)	wt. mono / wt. cubic	m/o cubic (y)	Equation of line	m/o CaO 100 % cubic	m/o 0 % cubic
A*	10	3.91	infinite	0	y= 8.49x - 33.18	15.7	3.91
A	10	12.5	0.47	72.9			
B*	17.5	7.51	infinite	0	y= 10.43x - 78.32	17.10	7.51
B	17.5	14.5	0.47	72.9			
C*	25	11.11	infinite	0	y= 13.38x - 148.7	18.6	11.11
C	25	17.5	0.235	85.5			

* Mole percent CaO at 0 mole percent cubic ZrO_2 was calculated from Equation (10).

APPENDIX D

QUANTITATIVE CHANGES IN CUBIC TO MONOCLINIC ZIRCONIA CONTENTS FOR LONG TERM FIRINGS

The weight ratio of cubic to cubic plus monoclinic zirconia contained in each of the long term fired samples was determined by X-ray diffraction and is recorded in Table 19.

Table 19. Ratios of Cubic to Cubic plus Monoclinic Zirconia for Compositions A, B, and C Fired at 900 °C and 1300 °C for up to 2000 Hours

Time (Hours)	900 °C			1300 °C		
	A	B	C	A	B	C
0	0.88	0.83	1.0	0.88	0.83	1.0
200	0.89	0.88	0.98	0.88	0.84	0.94
400	0.91	0.83	1.0	0.76	0.77	0.89
600	0.88	0.84	1.0	0.73	0.78	0.86
800	0.91	0.87	1.0	0.70	0.78	0.83
1000	0.91	0.84	1.0	0.72	0.69	0.81
1200	0.88	0.84	0.98	0.72	0.70	0.82
1400	0.89	0.81	0.97	0.71	0.69	0.88
1600	0.87	0.87	0.96	0.61	0.66	0.80
1800	0.89	0.85	0.97	0.72	0.71	0.81
2000	0.85	0.84	0.95	0.73	0.69	0.83

REFERENCES

1. A. S. Berezhnoi and R. A. Kordyuk, "Melting Diagram of the System $CaO-Al_2O_3-ZrO_2$," Dopovidi Akademii Nauk Ukrainskoi RSR, No. 10, 1344 - 1347 (1963).

2. A. S. Berezhnoi and R. A. (Kordyuk) Tarnopol'skaya, "Calcium Aluminozirconate - A New Hydraulic Binder," Izvestiya Akademii Nauk SSSR Neorganicheskie Materialy, 4 (12) 2151-2154 (1968).

3. R. A. Tarnopol'skaya and N. V. Gul'ko, "The $CaO-SrO-Al_2O_3-ZrO_2$ System and Its Importance for Refractories Technology," Ogneupory, No. 12, 38-42 (1967).

4. N. I. Voronin, V. S. Gorodetskii, and E. P. Fedorova, "Effect of Impurities on Stabilization of Zirconium Dioxide with Magnesium Dioxide and the Technical Properties of Zirconium Products," Trudy Vsesoyuznyi Inst. Nauch-Issled. Prockt. Rab. Ogneupory Prom., No. 37, 81 (1965). In Chemical Abstracts (66-98068p).

5. Antonio Cocco, "Sull'azione Esercitata da Piccole Percentuali de Al_2O_3 sui Limiti di Composizione della Fase con Struttura Cubica Constituita da CaO e ZrO_2," La Chimica e L'Industria, 42 (2) 142- 145 (1960).

6. Hiroyoshi Takagi, et al., Effects of Alumina on Sintering of Zirconia Stabilized with Calcia," Sprechsaal fuer Keramik, Glas, Baustoffe, 107 (13) 584-588 (1974).

7. Kenneth Shaw, Refractories and Their Uses. John Wiley & Sons, New York, 1972, p. 151.

8. Pol Duwez and Francis Odell, "Phase Relationships in the System Zirconia-Ceria," Journal of the American Ceramic Society, 33 (9) 274-283 (1950).

9. Pol Duwez, Francis Odell, and Frank H. Brown, Jr., "Stabilization of Zirconia with Calcia and Magnesia," Journal of the American Ceramic Society, 51 (10) 553-556 (1968).

10. Ronald C. Garvie, "The Cubic Field in the System $CaO-ZrO_2$," Journal of the American Ceramic Society, 51 (10) 553-556 (1968).

11. B. C. Weber, et al., "Observations on the Stabilization of Zirconia," Journal of the American Ceramic Society, 39 (6) 197-207 (1956).

12. A. M. Gavrish, et al., "X-Ray Diffraction Investigation of the Decomposition Solid Solutions Based on Zirconium Dioxide," Izvestiya Akademii Nauk SSSR Neorganicheskie Materialy, 5 (9) 1584 -1588 (1969).

13. W. D. Kingery, Introduction to Ceramics. John Wiley & Sons, New York, 1960, p. 151.

14. R. W. Nurse, J. H. Welch, and A. J. Mujumdar, "The CaO-Al_2O_3 System in a Moisture Free Atmosphere," Transactions of the British Ceramic Society, 64 409-418 (1965).

15. F. M. Lea and C. H. Desch, The Chemistry of Cement and Concrete, 2d ed. Edward Arnold & Co., London, 1956, p. 52.

16. D. Brooksbank, "Thermal Expansion of Calcium-Aluminate Inclusions and Relation to Tessellated Stresses," Journal of the Iron and Steel Institute, 208 495-499 (1970).

17. A. Auriol, Phase Diagrams for Ceramists, American Ceramic Society, Columbus, Ohio, 1964, p. 102, fig. 232.

18. Powder Diffraction File, Joint Committee on Powder Diffraction Standards, Philadelphia, 1960, cards 7-82 and 1-572.

19. G. R. Rigby and A. T. Green, "The Thermal Expansion Characteristics of the Calcium Aluminates and Calcium Ferrites," Transactions of the British Ceramic Society, 42 (5) 95-103 (1943).

20. Julian R. Goldsmith, "The Compound $CaO \cdot 2Al_2O_3$," Journal of Geology, 56 80-81 (1948).

21. B. Tavisci, "Constitution of Portland Cement Clinker," Tonindustrie-Zeitung 61 717-719 (1937).

22. E. R. Boyko and L. G. Wisnyi, "The Optical Properties and Structures of $CaO \cdot 2Al_2O_3$ and $SrO \cdot 2Al_2O_3$," Acta Crystallographica 11 444-445 (1958).

23. P. J. Baldock, et al., "X-Ray Powder Diffraction Data for Calcium Monoaluminate and Calcium Dialuminate," Journal of Applied Crystallography, 3 188-191 (1970).

24. Woldemar A. Weyl and Evelyn C. Marboe, The Constitution of Glasses, Interscience Publishers, New York, 1962, p. 30.

25. Hans W. Hennicke and Horst Vaupel, "The Stabilization of Zirconium Dioxide with Aluminum Dioxide," Tonindustrie-Zeitung, 94 45-50 (1970).

26. R. E. Thoma, "Determination of Phase Diagrams," Handbook of X-rays E. F. Kaeble, McGraw Hill, New York, 1964, chapter 20.

27. Leonid V. Azaroff, Elements of X-Ray Crystallography, McGraw-Hill, New York, 1968. p. 517.

28. J. K. Cochran, Private Communication, Georgia Institute of Technology, Atlanta, Ga., March, 1976.

29. S. W. Freiman, "Applied Stereology," c. 19 in Characterization of Ceramics, ed. L. L. Hench, Marcel Dekker, Inc., New York, 1971, p. 569.